GULU UNIVERSITY

Introduction to
Organic Chemistry

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by

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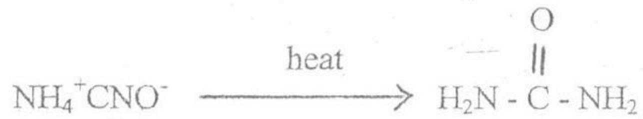
Functional derivatives of carboxylic acids

CHAPTER 1

INTRODUCTION

What is Organic Chemistry?

Organic chemistry was originally defined as the chemistry of substances formed by living matter. In other words, it was regarded as the chemistry of substances obtained from plant and animal parts. However, following Wohler's discovery that an organic compound, urea could be prepared in the laboratory by heating an inorganic salt, ammonium cyanate, the definition lost meaning.



$$NH_4^+CNO^- \xrightarrow{heat} H_2N-\overset{\overset{O}{\|}}{C}-NH_2$$

ammonium cyanate

urea

However, the term organic chemistry was retained to designate the branch of chemistry dealing with carbon compounds. These compounds include simple molecules like methane, ethyne (acetylene, which are used as fuels and as starting materials for the synthesis of other organic compounds; giant molecules like deoxyribonucleic acid (DNA), which contains all the genetic information for a given species; compounds like polyethene, polystyrene, rubber, cotton and nylon; petroleum products (petrol, grease, diesel, lubricating oil); drugs, dye, insecticides, explosives, photographic films - all of which are of great importance in everyday life.

Organic chemistry is also the foundation for the basic studies in botany, zoology, microbiology, nutrition, forestry; agriculture, veterinary medicine, human medicine, pharmacy, technology etc.

Organic chemistry can now be defined as the chemistry of carbon compound, usually containing the elements hydrogen, oxygen, nitrogen, halogens or sulphur and phosphorus.

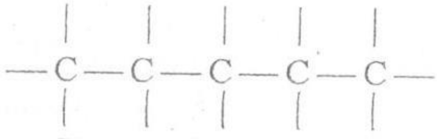
Diversity of organic compounds

Carbon is unique in that it can form a vast number of different compounds. This is because of:

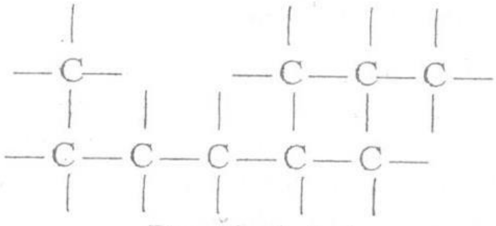
- the unusual strength of the carbon - carbon bond;
- the four valency electrons on the carbon atom that make it possible for carbon to combine with as many as four other atoms;
- the ability of carbon to combine with atoms of other non-metals (e.g. hydrogen, oxygen, nitrogen, halogens, sulphur and phosphorus);

- the possibility that carbon atoms can combine to form straight or branched chain or ring compounds.

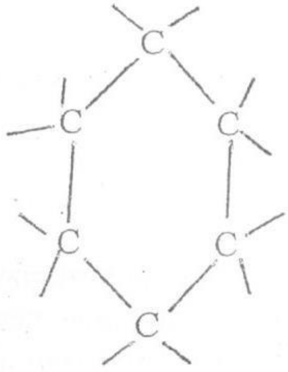
Examples



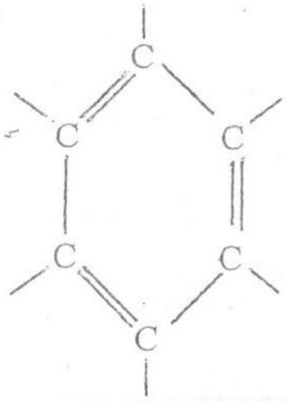
Straight chain



Branched chain

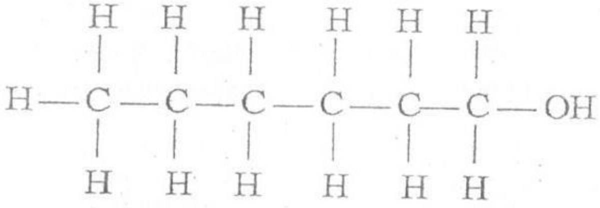


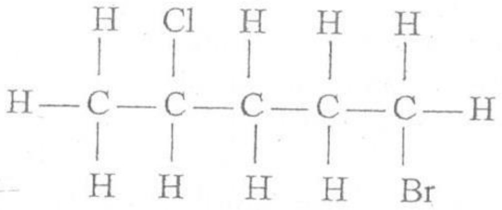
Ring

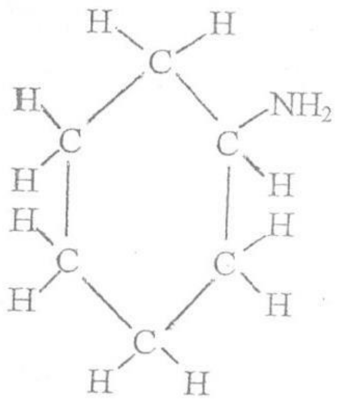


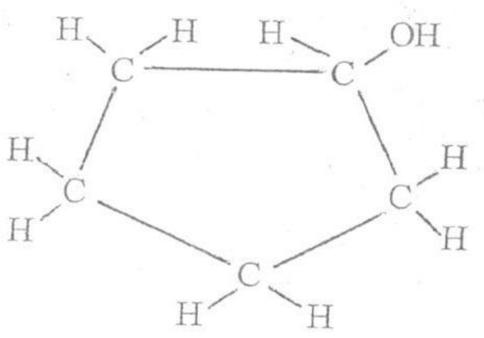
Benzene ring

These ring or chain structures may contain hydrogen or other non-metal atoms bonded to the remaining sites on the carbon atoms.









Some general characteristics of organic compounds

Most organic compounds are

- covalent and involves relatively few elements (mainly carbon, hydrogen, oxygen, nitrogen, sulphur, nitrogen and the halogens).
- low melting and boiling compounds.
- generally insoluble in water (except those containing hydroxyl, OH, groups, e.g. ethanol, sugar, etc.) but are soluble in organic solvents e.g. ether and benzene.
- varies in rate of reaction from slow to explosive and in most cases require catalysts.

Homologous series

A number of organic compounds can be placed in some series known as ***homologous series***, which have the following characteristics:

(a) Members of a homologous series can be represented by a general formula, for example, C_nH_{2n+2} for the alkanes.
(b) Each member of the series has a similar method of preparation and similar chemical properties to the other members.
(c) As the series is ascended, a methylene, $-CH_2-$, group is added to each successive member.
(d) As the methylene group is added, physical properties (for example, melting point, boiling point and density) change slightly.
(e) Several homologous series can be regarded as derived from alkanes, a hydrogen being replace by a functional group.

Functional group

Functional group is atom or group of atoms which impart specific chemical properties to the compounds containing then regardless of the nature of the hydrocarbon portion of the molecule.

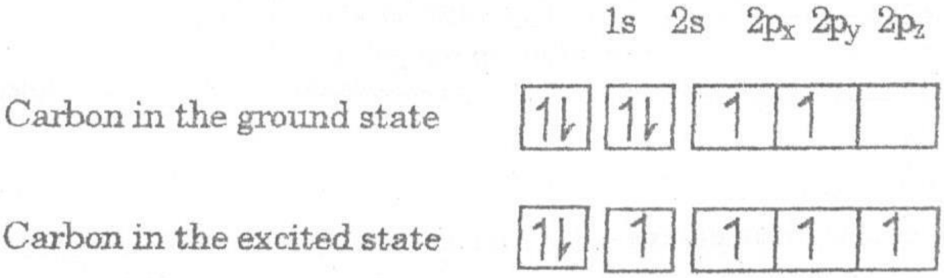
Organic compounds are usually classified according to functional groups. This is because all compounds containing the same functional group will have properties that are characteristic of that group.

ELECTRONIC CONFIGURATION OF CARBON ATOM AND HYBRIDISATION

Formation of carbon - carbon single bond (sp3 hybridisation)

The carbon atom has six electrons. They occupy 1s, 2s and 2p orbitals. When filling these orbitals, electrons always occupy the orbitals of the lowest energy first. The electronic configuration of a carbon atom is thus: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$.

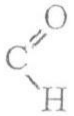
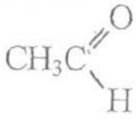
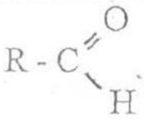
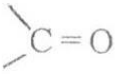
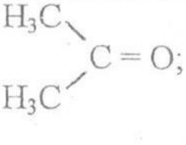
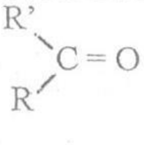
All the three 2p orbitals have the same energy and are called degenerate orbitals. According to the electronic configuration, carbon is expected to possess a valency of two but tetravalecy of carbon is a fundamental fact on which the whole structural organic chemistry has been built. We could promote one of the 2s electrons to an orbital of higher energy, but this alone would not explain the tetrahedral arrangement of the valence bonds about the carbon atoms. To explain the four equivalent tetrahedral valencies of carbon, it has been suggested that one of the 2s electrons is promoted to a 2p-orbital (p_z, for instance) and the three p-orbitals are then combined with the 2s orbital to give a set of four equivalent orbitals.



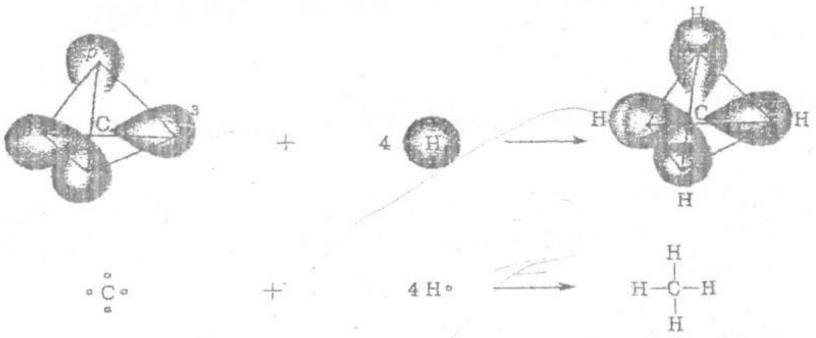
Or $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$ $1s2(sp^3)$

Thus we now have four equivalent hybridised orbitals with the same energy levels. These hybridised orbitals can combine to form a tetrahedral structure. When the carbon atom is joined to four other atoms, each of these four sp^3 hybridised orbitals of the carbon overlap with a suitable orbital of the atom to form four molecular orbitals arranged symmetrically around the carbon atom. The atoms are separated from each other by a tetrahedral angle of 109° 28'. This type of bond is known as a ***sigma- (σ-) bond.***

Examples of functional groups

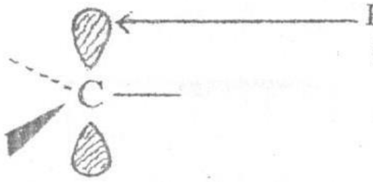
Name	*Structural features*	*Examples*
Alkanes	Hydrocarbons containing single bonds only	$H_3C - CH_3$; RH
Alkenes	Hydrocarbons containing a double bond between carbon atoms.	$H_2C = CH_2$ $CH_3CH = CHCH_3$ $RCH = CH_2$; $RCH = CHR'$
Alkynes (Acetylenes)	Hydrocarbons containing a triple bond between carbon atoms.	$HC \equiv CH$ $CH_3C \equiv CCH_3$ $RC \equiv CR'$; $RC \equiv CH$
Alkyl halides (Halogen compounds)	Aliphatic hydrocarbons in which or more hydrogen atom(s) is/are replaced by halogen atom(s)	CH_3CH_2Cl; RX (X = Cl, Br or I)
Alcohols	Aliphatic hydrocarbons in which or more hydrogen atom(s) is/are replaced by hydroxyl (OH) group(s)	CH_3CH_2OH; $CH_3CH(OH)CH_3$; RCH_2OH; R_2CHOH, R_3OH
Aldehydes	Compounds containing the group -  $-C(=O)H$ The carbonyl carbon is bonded to at least one hydrogen atom.	 $CH_3C(=O)H$  $R-C(=O)H$
Ketones	Compounds containing the carbonyl group with the carbonyl carbon bonded to two carbon atoms.  $>C=O$	 $(H_3C)_2C=O$;  $R'(R')C=O$
Carboxylic acids	Compounds containing the carboxyl group, $-CO_2H$	CH_3CO_2H; RCO_2H
Amines	Amines may be regarded as derivatives of ammonia containing a nitrogen atom bonded to at least one carbon atom	$CH_3CH_2NH_2$; RNH_2 $(CH_3CH_2)_2NH$; R_2NH $(CH_3CH_2)_3N$; R_3N

Formation of methane molecule



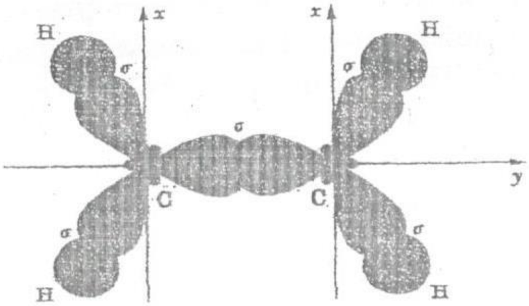
Formation of carbon-carbon double bond or sp^2 hybridisation

In the formation of the sp^2 hybridised carbon atom, one of the electrons in the 2s orbital is promoted to a 2p orbital as mentioned before. But in this case the electron remaining in the 2s combines or hybridises with only two of the 2p-orbitals to form three equivalent sp^2 hybridised orbitals. One electron remains as a p electron and is not involved in the hybridisation. The three sp^2 hybridised orbitals lie in a plain at 120° to each other and form σ-bonds joining the other atoms to the carbon atom. The remaining p orbital is at right angle to the plane of the three σ-bonds and extends above and below this plane.



Remaining p orbital which is not involved in the hybridisation

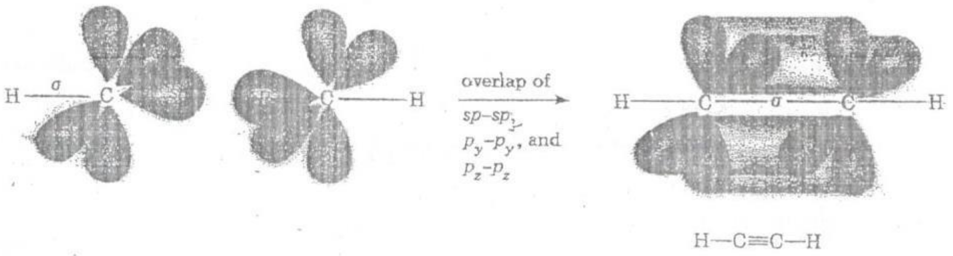
In a molecule like ethene, there are two adjacent carbon atoms each linked to three atoms by σ-bonds and each having one p-orbital which is not involved in the hybridisation. The p-orbitals are parallel to one another and can overlap one another laterally (since the distance between the two carbon atoms is very close) to form a further bond between the two atoms. This type of bond is a pi- (π-) bond. Thus we have three bonds of the σ-type mutually inclined at 120°, all in one plane, and one bond of the π-type forming an electron cloud above and below the plane of the six atoms.



The σ-bond framework of ethene based on sp^2 hybridised carbon atoms

Formation of a carbon-carbon triple bond or sp hybridisation

In the formation of carbon-carbon triple bond, one of the 2s electron is promoted to the 2p vacant orbital and only one of the p orbitals is hybridised with 2s orbital to form two sp hybridised orbitals to each other. These are at right angles at each other. Lateral overlap of the two orbitals leads to two π-bonds thus resulting in a cylindrical cloud of electrons around the two carbon atoms.

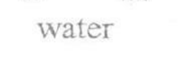


Overlapping of p-orbitals of ethyne

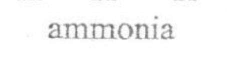
Polarity of covalent bonds

In a covalent bond formed between identical atoms, as in hydrogen molecule, the electron pair forming the σ-bond is shared equally between the two atoms. However, when two unlike atoms of different electronegativities form a single covalent bond, the electron pair is not shared equally between them. The atom which is more electronegative draws the electron pair closer to itself. For example, in the C-Cl bond, the chlorine atom which is more electronegative than the carbon atom draws the bonding electrons towards itself. As a result, the carbon atom becomes slightly positively charged and the chlorine atom is slightly negatively charged. The bond between carbon and chlorine is thus said to be polar or to possess polarity. Other examples of molecules with polar bonds are shown below (δ denotes partial charge).

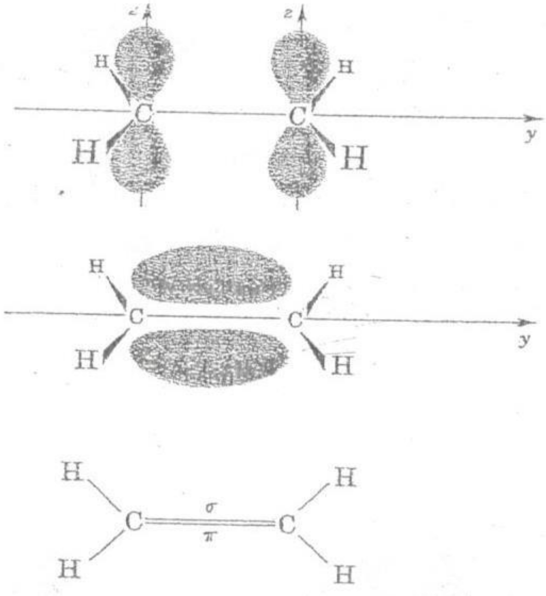
$H^{\delta+}–Cl^{\delta-}$
hydrogen
chloride



water

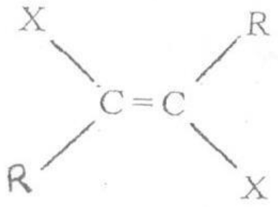


ammonia



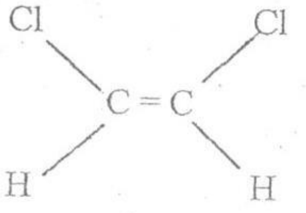
Overlapping of p-orbitals of ethene

In this structure there is restriction of rotation about carbon - carbon axis. Hence structures of the type

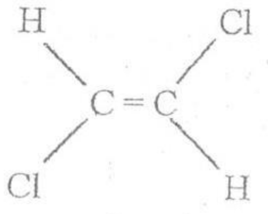


may exist in two geometric forms (*cis*- the same substituents are on the same side and *trans*- the same substituents are on opposite sides).

For example:



cis



trans

A molecule is said to be polar if the negative charge does not coincide with the centre of the positive charge. Such a molecule constitute a dipole (symbolised --|----->), the arrow points from the positive to the negative end.

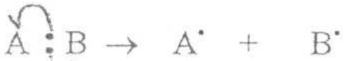
ORGANIC CHEMICAL REACTIONS

Breaking of covalent bonds

There are two ways in which electrons may be redistributed when a covalent bond is broken.

(a) Homolytic cleavage

In the homolytic cleavage, the bond is broken symmetrically and each atom retains one electron. The resultant species contain unpaired electrons and are known as ***radicals***. For example, for a σ-bond between A and B,



$$A:B \rightarrow A^{\cdot} + B^{\cdot}$$

two separate
radicals

Most carbon radicals are uncharged species, although both anion and cation radicals are known. Reactions proceeding by homolytic cleavage are frequently found in homogeneous (one phase present) gas reactions and also in reaction which occur in solvents of low ionising power. The reactions which tend to be chain reactions are promoted or catalysed by:

- short wavelength light (e.g. ultraviolet);
- high temperatures;
- oxygen;
- peroxides (both organic and inorganic).

(b) Heterolytic cleavage

In this type of cleavage, the bond is broken unsymmetrically. One of the atoms retains both electrons which previously formed the bond. The atom thus becomes negatively charged (anion) and the other atom become positively charged (cation). For example,

$$A:B \rightarrow A^{+} + B^{-}$$

carbon ions

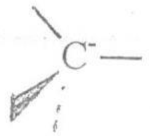
If A and B are different types of atoms, the direction of electron movement depends on the relative electronegativity of the two atoms i.e. electrons will shift towards the more electronegative atom. If A and B are the same kind, (e.g. C-C) the direction depends on:

- nature of the other atoms or group of atoms attached to each atom.
- condition of the reaction (solvent, temperature and reactants).
- relative energy content of the excited state.

Heterogeneous cleavage of bonds is common in reactions that take place in solvents of high ionising power (e.g. water, pyridine, etc.) and is promoted or catalysed by ionic or polar catalysts (e.g. H^+, ^-OH, metal ions and $C_2H_5O^-$).

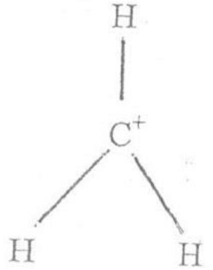
Carbanions

Carbanions are carbon anions. They are formed by the removal of one of the groups (or atoms) attached to a carbon atom without removing the bonding pair of electrons. They are probably pyramidal.



Carbonium ions

Carbonium ions are carbon cations. They may be regarded as fragments of molecules in which a group and bonding electrons have been removed from one of the carbon atoms. The positively charged carbon atom is sp^2 hybridised. The ion should thus be planar.

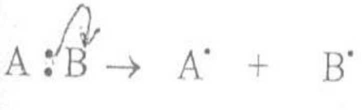


Methyl carbonium ion

Reaction mechanism

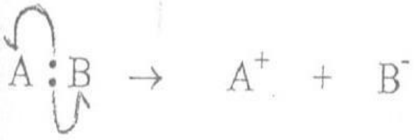
Reaction mechanism is a very useful concept in organic chemistry. It is a step by step description of events that take place at molecular level during a reaction.

The following conventions are used in writing reaction mechanisms:
(i) Arrows are used to show the direction of electron(s) during a reaction.
(ii) Single-barbed arrow, ⇀, shows the movement of an unpaired electron.



$A:B \rightarrow A^{\bullet} + B^{\bullet}$

(iii) Double-barbed arrow, , shows the movement of an electron pair



$A:B \rightarrow A^{+} + B^{-}$

The arrow must start from an electron or an electron pair and point to where the electron is going to form a bond to the atom to which is going to be deposited. For example, in the reaction above, the bonding pair of electrons between A and B have been transferred to B and A is positively charged while B is negatively charged.

CHAPTER 2

ALKANES

Hydrocarbons

Hydrocarbons are compounds that contain carbon and hydrogen only.

Classification of hydrocarbons

Hydrocarbons may be classified as

(a) aliphatic hydrocarbons, which are open chain compounds. These may again be subdivided into:
   (i) alkanes (or paraffins) - saturated open chain hydrocarbons.
   (ii) alkenes (or olefins) - open chain hydrocarbons containing at least one carbon - carbon double bond.
   (iii) alkynes (or acetylenes) - open chain hydrocarbons containing at least one carbon-carbon triple bond.

(b) aromatic hydrocarbons - contain a benzene ring(s).

(c) alicyclic hydrocarbons - contain rings which are not benzene rings.

ALKANES

Alkanes are open chain compounds which contain carbon and hydrogen only. There are no double bond or triple bond between carbon atoms. They may be represented by the general formula C_nH_{2n+2} or RH.

Sources of alkanes

The main sources of alkanes are:

(a) Natural gas - these contain mainly methane with smaller amounts of other low molecular gases such propane and butane.
(b) Petroleum fractions contain a wide range of alkanes ranging from low molecular mass gases to high molecular mass waxy solids (usually C_2 to C_{40}. The components of petroleum are separated by fractional distillation in a process known as ***refining***.

Nomenclature of straight chain alkanes

The C_1 to C_4 alkanes are given trivial names. Those containing more than four carbon atoms in a chain are given names in which the prefix show the number of carbon atoms in the chain (in Greek or Latin), followed by the ending ***ane*** to denote alkane.

Examples

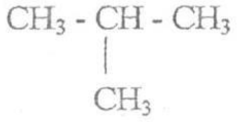
Structural formula	*Name*
CH_4	Methane
CH_3CH_3	Ethane
$CH_3CH_2CH_3$	Propane
$CH_3CH_2CH_2CH_3$	Butane
$CH_3(CH_2)_3CH_3$	Pentane
$CH_3(CH_2)_4CH_3$	Hexane
$CH_3(CH_2)_5CH_3$	Heptane
$CH_3(CH_2)_6CH_3$	Octane
$CH_3(CH_2)_7CH_3$	Nonane
$CH_3(CH_2)_8CH_3$	Decane

Nomenclature of branched chain alkanes

The basic feature of the nomenclature of alkanes is that the molecule is regarded as an alkyl derivative of the longest continuous chain of carbon atoms in the molecule. The nomenclature is governed by a set of rules drawn up by the conference of International Union of Pure and Applied Chemistry (IUPAC) and the names derived from such rule are known as systematic names.

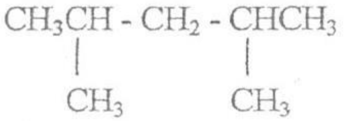
Rules for naming branched chain alkanes

1. Choose the longest continuous chain of carbon atoms and this determines the base name of the alkane. For example,



$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3$

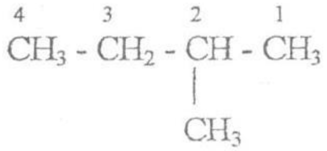
is a propane and not a butane and



$CH_3\underset{\underset{CH_3}{|}}{CH} - CH_2 - \underset{\underset{CH_3}{|}}{CH}CH_3$

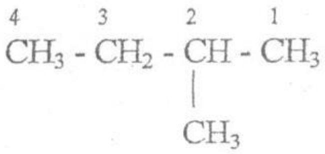
is a pentane and not a pentane

2. Number the longest chain beginning with the end nearest to the branching. For example,



$\overset{4}{CH_3} - \overset{3}{CH_2} - \underset{\underset{CH_3}{|}}{\overset{2}{CH}} - \overset{1}{CH_3}$

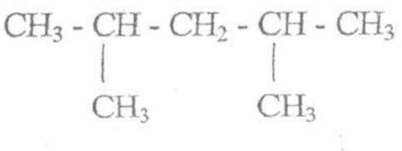
3. Use the numbers obtained by applying rule 2 above to indicate the location of the substituent. For example, in the structure below the methyl substituent is on the carbon atom numbered 2.



$\overset{4}{CH_3} - \overset{3}{CH_2} - \underset{\underset{CH_3}{|}}{\overset{2}{CH}} - \overset{1}{CH_3}$

In writing the name of the alkane, the position of the substituent is written first, followed by a dash then the name of the substituent (methyl in this case) and the name of the alkane (the longest chain) written as one word. The above alkane is therefore called 2-methylbutane.

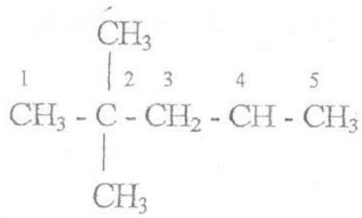
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example,



$\overset{1}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{2}{CH}} - \overset{3}{CH_2} - \underset{\underset{CH_3}{|}}{\overset{4}{CH}} - \overset{5}{CH_3}$

is 2,4-dimethylpentane.

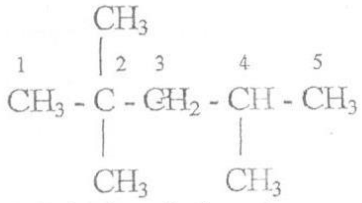
5. When two or more substituents are present on the same carbon atom, use that number of the carbon on which the substituents appear twice.



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH-CH_3$

2,2-dimethylpentane

6. When two or more substituents are identical, indicate this by the use of the prefix *di-*, *tri-*, *tetra,* etc. For example,



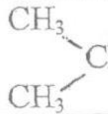
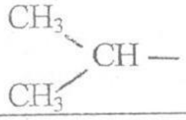
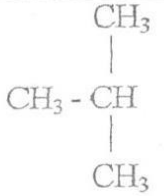
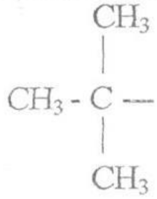
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2,2,4-trimethylpentane

Nomenclature of alkyl groups

Alkyl groups are derived from alkanes by the removal of one of the hydrogens. Their names end in ***yl*** instead of the last ***ane*** in the name of the corresponding alkane.

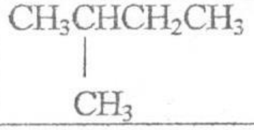
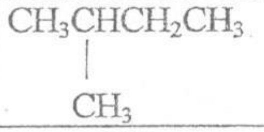
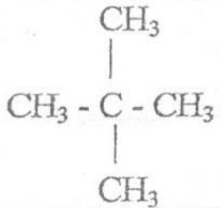
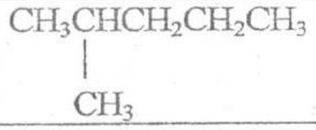
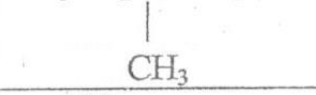
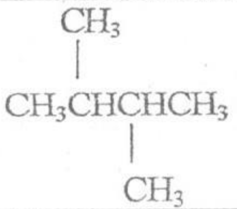
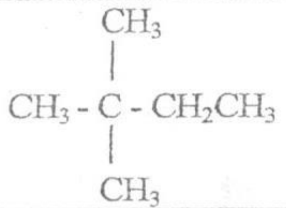
Examples

Alkane	***Name of alkane***	***Alkyl group***	***Name of alkyl group***
CH_4	Methane	CH_3 —	Methyl
CH_3CH_3	Ethane	CH_3CH_2 —	Ethyl
$CH_3CH_2CH_3$	Propane	$CH_3CH_2CH_2$ —	Propyl
	Propane		*iso*-Propyl
 $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{CH}}$	*tertiary*-Butane (2-methylpropane)	 $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}$ —	*tertiary*-Butyl (*ter*-butyl)

Physical properties of alkanes

The melting points and boiling points of alkanes increase with increase in molecular mass. Thus, C_1 - C_4 alkanes are gases, C_5 - C_{17} are liquids while the with more than 17 carbon atoms are waxy solids at room temperature.
Branched chain alkanes tend to have lower boiling points than the straight isomers (See the Table below). (Isomers are compounds with the same molecular formula but with different molecular structures).

Boiling and melting points of some straight chain and branched chain alkanes.

Molecular formula of alkane	***Structural formula***	***Melting point (°C)***	***Boiling point (°C)***
C_4H_{10}	$CH_3CH_2CH_2CH_3$	-138	0.5
C_4H_{10}	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	-159	-12
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	-130	36
C_5H_{12}	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	-160	28
C_5H_{12}	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$	-20	9.5
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	-19	68
C_6H_{14}	 $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_2CH_3$	-154	60
C_6H_{14}	 $CH_3CH_2\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	-118	63
C_6H_{14}	 $CH_3\overset{\overset{CH_3}{\vert}}{C}H\underset{\underset{CH_3}{\vert}}{C}HCH_3$	-129	58
C_6H_{14}	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_2CH_3$	-98	49

Density

Alkanes are the least dense of all group of organic molecules. They all have densities less than 1.00 and therefore float on water. Within the series, density increases with increase in molecular mass of alkanes.

Solubility

Alkanes are soluble in non-polar solvents like ether, benzene and other alkanes but are insoluble in water.

Physical constants of some straight chain alkanes

Number of carbon atoms	***Name of alkane***	***Boiling point (deg. C)***	***Melting point (deg. C)***	***Density***
1	Methane	-161.5		
2	Ethane	-88.6		
3	Propane	-42		
4	Butane	-0.5		
5	Pentane	36	-130	0.626
6	Hexane	69	-95	0.65
7	Heptane	98.4	-91	0.684
8	Octane	125.7	-57	0.703
9	Nonane	151	-54	0.718
10	Decane	174	-30	0.73
11	Undecane	196	-26	0.74
12	Dodecane	216	-10	0.749
13	Tridecane	243	-5.5	0.756
14	Tetradecane	253.5	6	0.763
15	Pentadecane	270.5	10	0.769
16	Hexadecane	287	18	0.773
17	Heptadecane	303	22	0.778
18	Octadecane	305 - 307	28	0.777
19	Nonadecane	330	32	0.777
20	Eicosane	343	38.8	0.789

General methods for the preparation of alkanes

members of compounds belonging to a particular homologous series can normally be prepared by a number of similar methods. The methods are known as the general methods for the preparation of that particular series. There are also some special methods by which particular members can be prepared.

Preparation from carboxylic acids

(a) From sodium salts of carboxylic acids and soda-lime

Alkanes can be prepared by heating a sodium salt of a carboxylic acid with soda-lime. Soda-lime is a mixture of sodium hydroxide and calcium oxide. The carbon dioxide liberated during the reaction reacts with sodium hydroxide to form sodium carbonate. Reactions in which carbon dioxide is eliminated from a molecule of an organic compound is known as ***decarboxylation*** reaction.

$$CH_3CO_2^-Na^+ \;+\; NaOH \xrightarrow{heat} CH_4 \;+\; Na_2CO_3$$

$$CH_3CH_2CO_2^-Na^+ \;+\; NaOH \xrightarrow{heat} H_3C-CH_3 \;+\; NaCO_3$$

$$RCO_2^-Na^+ \;+\; NaOH \xrightarrow{heat} RH \;+\; NaCO_3$$

The yield of alkane decreases with increase in the chain length of the carboxylic acid.

(b) From the electrolysis of sodium or potassium salts of carboxylic acids (Kolbe's method

When an aqueous solution of a sodium or potassium salt of a carboxylic acid is electrolysed, an alkane is liberated at the anode together with carbon dioxide.

$$2\,RCO_2^- \;\; -2e \;\rightarrow\; R-R \;+\; CO_2$$

For example, electrolysis of a solution of sodium ethanoate will give ethane and carbon dioxide.

$$2CH_3CO_2^- \;\; -2e \;\rightarrow\; H_3C-CH_3 \;+\; CO_2$$

From alkyl halides

(a) Reduction of alkyl halides

(i) Alkane can be prepared by the reduction of an alkyl halide using copper-zinc couple in ethanol. The copper-zinc couple reacts with ethanol to form nascent hydrogen which is required for the reduction.

$$RX + 2[H] \xrightarrow[\text{ethanol}]{\text{Cu-Zn couple}} RH + HX$$

(ii) Alkanes can also be obtained when an alkyl halide is reduced using lithium aluminium hydride in sodium dried ether as solvent.

$$4RX + LiAlH_4 \xrightarrow{\text{dry ether}} 4RH + LiAlX_4$$

(b) Reaction of an alkyl halide with sodium (Wurtz reaction)

Alkyl halides react with metallic sodium in sodium dried ether as solvent to form alkanes.

$$2RX + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$$

$$2CH_3CH_2CH_2Br + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

Higher yields are obtained with alkanes with higher molecular masses.

The method is useful for the preparation of alkanes with even number of carbon atoms.

From alkenes

The reactions leading to the formation of alkanes from alkenes is discussed under hydrogenation of alkenes.

From alkynes

The reactions leading to the formation of alkanes from alkenes is discussed under hydrogenation of alkynes.

REACTIONS OF ALKANES

Alkanes are generally unreactive. Reasons:

- the C - C and C - H bonds are strong i.e. they do not break easily unless alkanes are heated to high temperatures or are subjected to radiation of high energy, for example ultraviolet radiation.
- Carbon and hydrogen have nearly the electronegativity values. Therefore the C - H are only slightly polarised. Consequently alkanes are not affected by most bases.
- There are unshared electrons in alkanes. Therefore alkanes are not attacked by acids.

However, under certain drastic conditions (high temperatures, presence of ultraviolet radiation), alkanes do undergo few reactions to form mixtures of products. The reactions are usually free radical chain reactions.

(a) Combustion of alkanes

Alkanes burn in oxygen (air) to form carbon dioxide and water. The reaction is accompanied by liberation of energy. Therefore alkanes are used as fuels.

$$C_nH_{2n+2} \quad + \quad (3n+1)O_2 \quad \rightarrow \quad nCO_2 \quad + \quad (n+1)H_2O$$

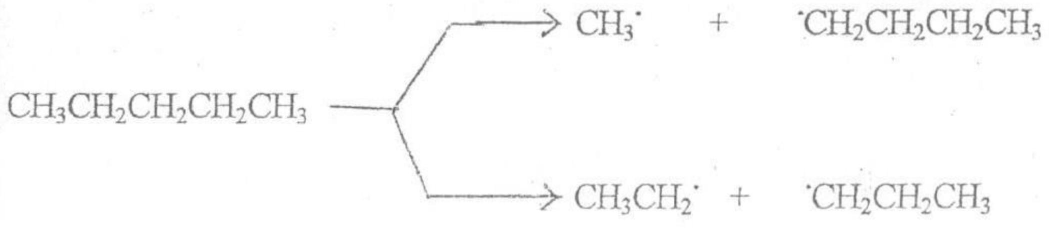
For example:

$$CH_4 \ + \ 2O_2 \quad \rightarrow \quad CO_2 \ + \ 2H_2O \qquad + \ \text{heat}$$

(b) Pyrrolysis (Cracking) of alkanes

Pyrrolysis is a process by which a molecule is broken up by heat.

When alkanes are pyrrolised, the C - C bonds are broken to give smaller alkyl radicals.



The alkyl radicals formed can react in the following manner:

(i) Recombination to form an alkane mixtures of different alkanes:

$CH_3^{\cdot} \ + \ {}^{\cdot}CH_3 \ \rightarrow \ CH_3CH_3$

$CH_3^{\cdot} \ + \ {}^{\cdot}CH_2CH_3 \ \rightarrow \ CH_3CH_2CH_3$

$CH_3CH_2^{\cdot} \ + \ {}^{\cdot}CH_2CH_2CH_2CH_3 \ \rightarrow \ CH_3CH_2CH_2CH_2CH_2CH_3$

(ii) Disproportionation - one alkyl radical transfer a hydrogen atom to another alkyl radical to form an alkane and an alkene.

$CH_3CH_2^{\cdot} \ + \ {}^{\cdot}CH_2CH_2CH_3 \ \rightarrow \ CH_3CH_3 \ + \ H_2C = CHCH_3$

Pyrrolysis results in the conversion of a large alkane molecule to smaller alkanes and alkene molecules. The reaction is not useful in the laboratory because a mixture of products id formed.

(c) Halogenation of alkanes

Alkanes react with halogens when heated (250° - 400°) or in the presence of ultraviolet light to form a mixture of products which are difficult to separate there not useful for the synthesis of alkyl halides.

Reactivity: fluorine > chlorine > bromine > iodine.

Reaction with fluorine is explosive and normally the reaction mixture is diluted with inert gas e.g. nitrogen.

Iodine does not react.

Reaction of chlorine with methane

The hydrogen atoms of methane are replaced by chlorine atoms when a mixture of methane and chlorine is exposed to ultraviolet radiation (e.g. bright sunlight). The reaction may become explosive and usually give a mixture of products.

$$CH_4 \xrightarrow[h\nu]{Cl_2} \underset{\substack{+\\HCl}}{CH_3Cl} \xrightarrow[h\nu]{Cl_2} \underset{\substack{+\\HCl}}{CH_2Cl_2} \xrightarrow[h\nu]{Cl_2} \underset{\substack{+\\HCl}}{CHCl_3} \xrightarrow[h\nu]{Cl_2} CCl_4 \ + \ HCl$$

Mechanism

Step 1

The initial step involves the dissociation of chlorine molecule homolytically into chlorine atoms (radicals). The light provides the energy required to break the bond. This step initiate the formation of free radical to start the chain reaction and is therefore called ***chain initiation step***.

$$Cl : Cl \xrightarrow[\text{(or UV light)}]{\text{heat}} 2Cl^{\cdot} \qquad \text{Chain initiation step.}$$

Step 2

The chlorine radical thus formed is very reactive and will attack a of methane and detaches a hydrogen atom with one electron, leaving behind the odd electron fragment $^{\cdot}$CH3, a methyl radical.

$$Cl^{\cdot}\ H : CH_3 \rightarrow \overset{HCl}{\cancel{ClH}} + {}^{\cdot}CH_3$$

Step 3

The methyl radical formed is also extremely reactive. Thus, on colliding with chlorine molecule, detaches a chlorine atom and leaves a chlorine radical behind.

$$H_3C^{\cdot}\ Cl : Cl \rightarrow H_3CCl + {}^{\cdot}Cl$$

The chlorine radical can now attack another methane as in step 2 and so the chain of the reaction continues.

In steps 2 and 3, more radicals are formed to continue the chain reaction and it is therefore called ***chain propagation step***.

Initiation by one chlorine radical is enough to bring about the reaction of hundreds or thousands of molecules of chlorine and methane. It would in fact bring about complete reaction of all the materials present had it not been due to the fact that occasionally the chlorine radicals or methyl radicals, which are the chain carriers are destroyed by the chain terminating step.

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Step 4: Chain terminating steps

$H_3C^{\cdot} + {}^{\cdot}Cl \rightarrow H_3C - Cl$

$Cl^{\cdot} + {}^{\cdot}Cl \rightarrow Cl - Cl$

$H_3C^{\cdot} + {}^{\cdot}CH_3 \rightarrow H_3C - CH_3$

However, since the concentration of $H_3C^{\cdot}$ and ${}^{\cdot}Cl$ are low, these reactions are infrequent. It is most likely that the radicals will collide with the molecules to continue the chain according to Steps 2 and 3.

The reaction between bromine and alkanes by similar mechanism is difficult. It is found from experiment that a mixture of methane reacts very slowly at room temperature in the presence of ultraviolet light. The mixture has to be heated if the reaction is to proceed at a reasonable rate. The explanation here is that the enthalpy change for the reaction between bromine radical and methane is endothermic (c.f. Step 2 above for chlorination) and the reaction is energetically unfavourable.

$$Br^{\cdot}\ H : CH_3 \rightarrow BrH + {}^{\cdot}CH_3 \qquad \Delta H = +61\ Jmol^{-1}$$

With fluorine, the reaction is explosive and the reaction mixture has to be diluted with an inert gas, for example, nitrogen gas.

Iodine does not react. The explanation is beyond the scope of this book.

(d) Nitration

Alkanes react with nitric acid in vapour phase to form nitroalkanes.

$$RH + HNO_3 \xrightarrow{\text{About } 450^{\circ}} R\text{-}NO_2 + H_2O$$

(e) Sulphonation

When higher alkanes are treated with fuming sulphuric acid, alkyl sulphonic acids are formed i.e. a hydrogen atom of the alkane is replaced by a sulphonic acid group, -SO_2OH.

$$RH + HO\text{-}SO_2OH \rightarrow R\text{-}SO_2OH + H_2O$$

CHAPTER 3

ALKENES

Introduction

Alkenes are hydrocarbons that contain a double bond between two carbon atoms. They are described as unsaturated as compared to the alkanes which do not contain carbon-carbon double bonds and are therefore said to be saturated. Alkenes can be represented by general formula C_nH_{2n} or $RCH = CH_2$ or $RCH = CHR'$.

Nomenclature of alkenes

The IUPAC rules for naming alkenes are very similar to those for naming alkanes.

1. Choose the longest chain of carbon atoms containing the double bond and change the ending of name of the alkane of identical length from ***ane*** to ***ene*** and this will form the base name for the alkene.

   For example

   $CH_3CH = CH_2$ is propene and $H_2C = CH_2$ is ethene.

2. Number the chain beginning with the end nearest to the first carbon containing the first double bond.

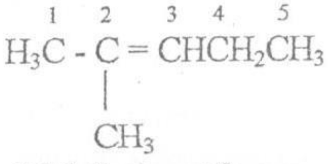
   $$\overset{1}{H_2C} = \overset{2}{C}\overset{3}{H}\overset{}{CH_2}\overset{4}{CH_3}$$

   But-1-ene

   $$\overset{1}{CH_3}\overset{2}{CH} = \overset{3}{CH}\overset{4}{CH_2}\overset{5}{CH_3}$$

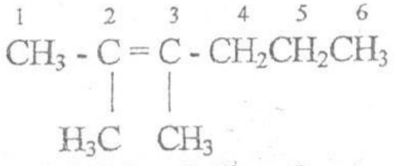
   Pent-2-ene

3. Indicate the location of the substituents by the numbers of the carbon atoms to which they are bonded.



$$\overset{1}{H_3C} - \underset{CH_3}{\overset{2}{C}} = \overset{3}{C}\overset{}{H}\overset{4}{CH_2}\overset{5}{CH_3}$$

2-Methylpent-2-ene



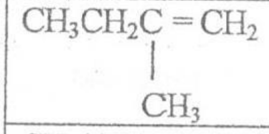
$$\overset{1}{CH_3} - \underset{H_3C}{\overset{2}{C}} = \underset{CH_3}{\overset{3}{C}} - \overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$$

2,3-Dimethylhex-2-ene

Physical properties of alkenes

The physical properties of alkenes are similar to those of alkanes. The melting points and the boiling points of alkenes are, however, lower than those of the corresponding alkanes. The solubilities of alkenes in polar solvents are generally higher than those of alkanes.

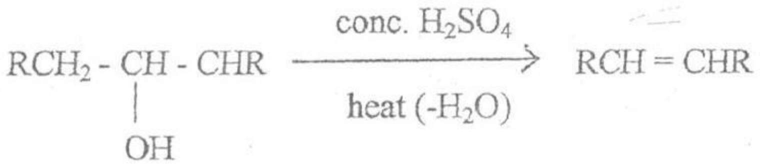
Physical constants of some alkenes

Formula	*Name*	*Melting point (deg. C)*	*Boiling point (deg. C)*	*Density (g per ml)*
$H_2C=CH_2$	Ethene	-169	-104	0.384
$CH_3CH=CH_2$	Propene	-185	-47	0.514
$CH_3CH_2CH=CH_2$	But-1-2ne	-185	-6.3	0.595
$CH_3CH=CH\,CH_3$	But-2-ene (*cis*)	-139	3.7	0.621
$CH_3CH=CH\,CH_3$	But-2-ene (*trans*)	-106	0.9	0.604
$CH_3CH_2CH_2CH=CH_2$	Pent-1-ene	-165	30	0.641
 $CH_3CH_2C(CH_3)=CH_2$	2-Methylbut-1-ene	-138	31	0.650
$CH_3(CH_2)_3CH=CH_2$	Hex-1-ene	-140	63	0.673
$CH_3(CH_2)_4CH=CH_2$	Hept-1-ene	-119	94	0.697

Methods for the preparation of alkenes

From alcohols

Alkenes are formed when alcohols are heated with excess concentrated sulphuric acid or concentrated orthophosphoric acid. The temperature of the reaction depends the structure of the alcohol. The reaction is regarded as the removal of a water molecule from a molecule of an alcohol. Hence the reaction is called dehydration of alcohols



$$RCH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CHR \xrightarrow[\text{heat }(-H_2O)]{\text{conc. }H_2SO_4} RCH=CHR$$

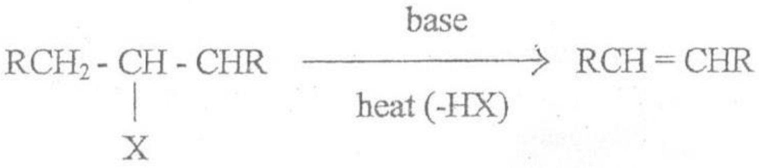
$$CH_3CH_2CH_2OH \xrightarrow[180^\circ\text{ C }(-H_2O)]{\text{conc. }H_2SO_4} CH_3CH=CH_2$$

The dehydration of alcohols to give alkenes can also be brought about by passing the vapour of the alcohol over heated alumina.

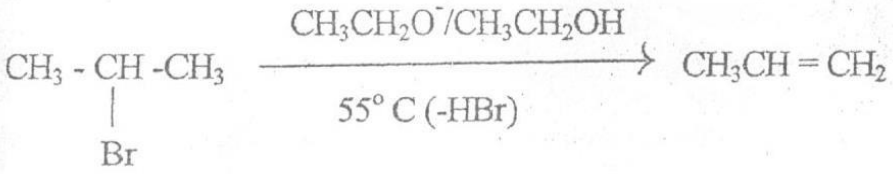
$$CH_3CH_2OH \xrightarrow[\text{heat}]{Al_2O_3} H_2C=CH_2$$

From alkyl halides

(i) Alkenes are prepared from alkyl halides by heating an alkyl halide with a strong base. For example, ethanolic potassium hydroxide solution, which contains the ethoxide ion, $CH_3CH_2O^-$, as the base. Ethoxide is a stronger base than hydroxide ion.



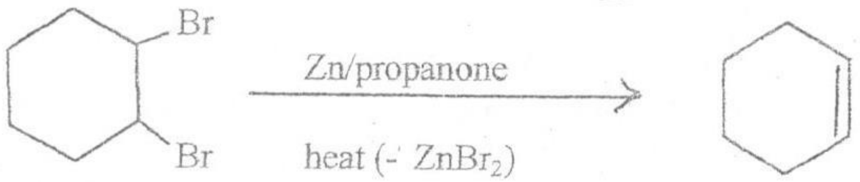
$$RCH_2-\underset{\displaystyle X}{\underset{|}{CH}}-CHR \xrightarrow[\text{heat }(-HX)]{\text{base}} RCH=CHR$$



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[55^\circ\text{ C }(-HBr)]{CH_3CH_2O^-/CH_3CH_2OH} CH_3CH=CH_2$$

The reaction is known as ***dehydrhalogenation*** since it involves the removal of a hydrogen halide from a molecule of the alkyl halide.

(ii) When a dihalogen alkane containing two halogen atoms on neighbouring carbon atoms is heated with zinc, an alkene is formed and the two halogen atoms are removed from the molecule.



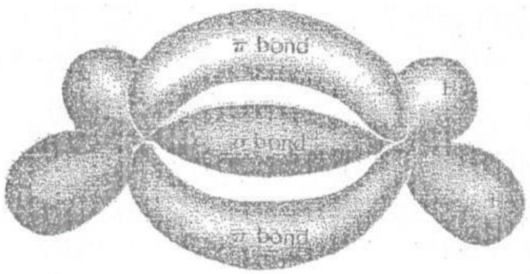
All the above reactions in which carbon-carbon bonds are formed are known as ***elimination*** reactions.

On the industrial scale, alkenes are normally obtained by the cracking of petroleum products.

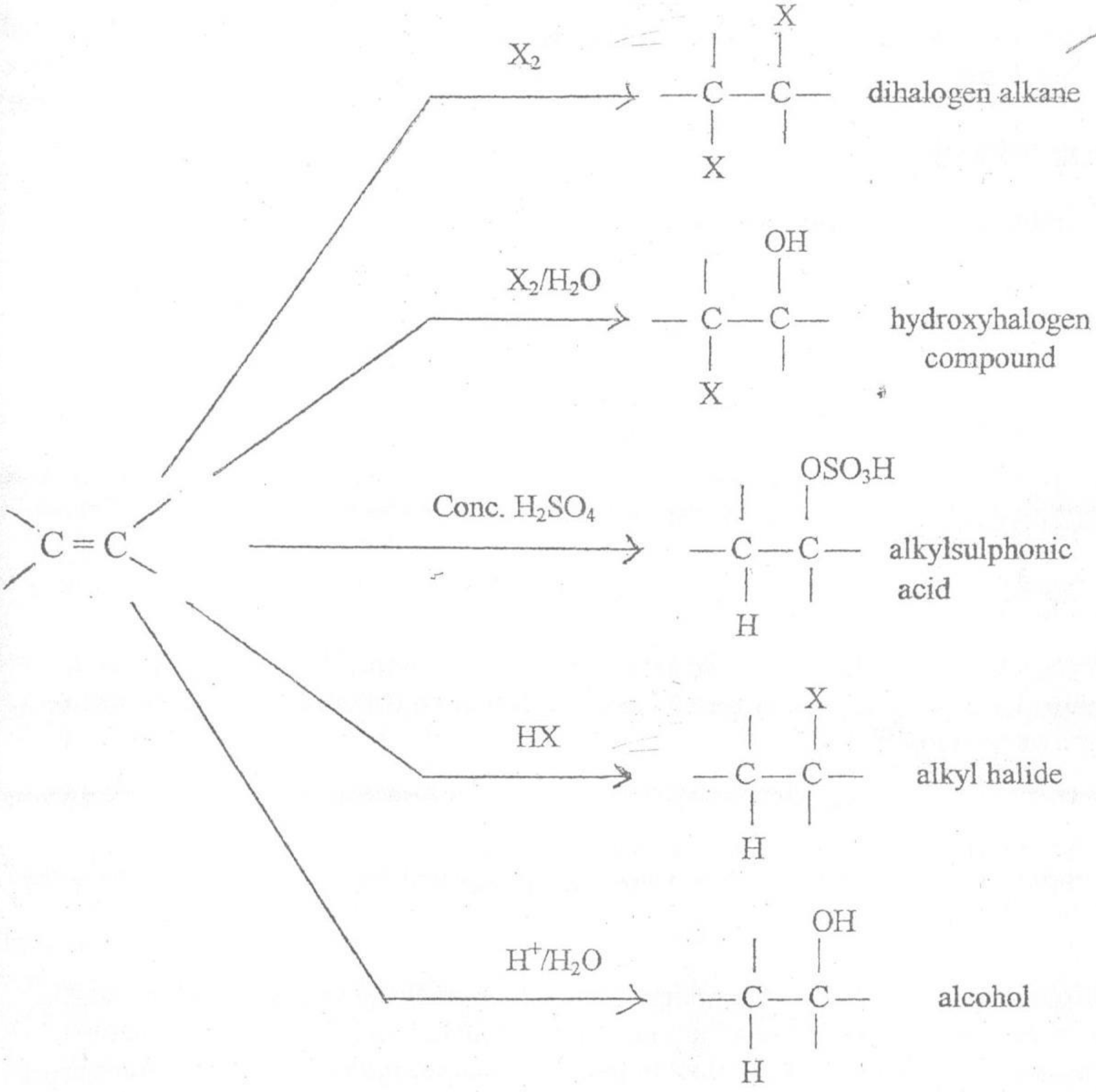
Reactions of alkenes

Alkenes are more reactive than alkanes. This is because the electron cloud of the two electrons in the π-orbital are not concentrated between the nuclei of the two carbon atoms containing them. They are more exposed and are energetically more available for reaction. Thus reagents that act to acquire electrons, called electrophilic reagents are particularly suitable for reaction with alkenes.

Reagents that are primarily electron-donating (electron rich) are poor reagents for reaction with alkenes, unless the latter contains a strong electron withdrawing substituents.



Alkene therefore undergo electrophilic addition reactions with various electrophilic reagents as outlined below.



Addition of hydrogen

Alkenes react with gaseous hydrogen in the presence of a catalyst to form alkanes. The reaction takes place at room temperature. Nickel, platinum or palladium can be used as catalysts. The reaction is known as ***hydrogenation*** and is not an electrophilic addition reaction. Since one double bond reacts with one mole of hydrogen, the reaction can be used to determine the number of double bonds in a molecule containing carbon - carbon double bonds.

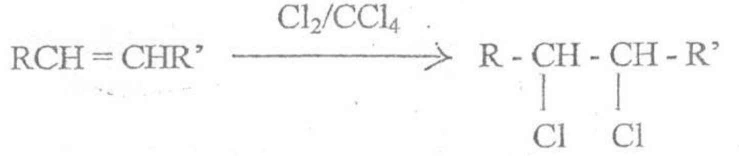
$$RCH = CHR' \xrightarrow{H_2/Ni} RCH_2CH_2R'$$

$$CH_3CH=CHCH_3 \xrightarrow{H_2/Ni} CH_3CH_2CH_2CH_3$$

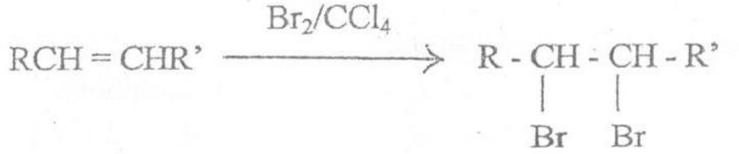
but-2-ene butane

Addition of halogens

Chlorine and bromine add readily to alkene double bonds.



$$RCH=CHR' \xrightarrow{Cl_2/CCl_4} R-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-R'$$



$$RCH=CHR' \xrightarrow{Br_2/CCl_4} R-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-R'$$

For example when ethene is passed into bromine solution in tetrachloromethane at room temperature, 1,2-dibromoethane is formed and the colour of the solution changes from reddish-brown to colourless.

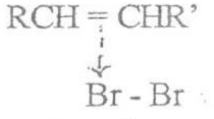
$$CH_2=CH_2 \xrightarrow{Br_2/CCl_4} Br-CH_2CH_2-Br$$

ethene 1,2-dibromoerhane

The decolouration of a solution of bromine in tetrachloromethane by alkenes id the cold is used as a test for the presence of a carbon - carbon double bond. The reaction can also be used to determine the number of double bonds in alkene since one mole of bromine reacts with one double bond.

Mechanism for the addition of bromine to alkenes (electrophilic addition reaction)

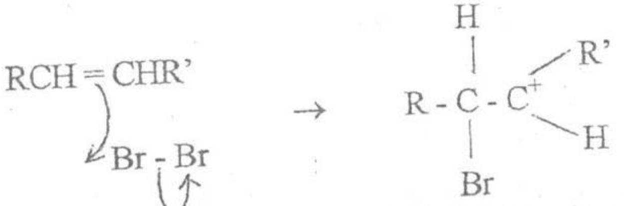
The first step in the electrophilic addition to carbon - carbon double bond can be regarded as the formation, by the electrophilic reagent, of a loose complex with the π-electrons of the double bond prior to the addition reaction. The complexes are called charge-transfer complexes (or π-complexes).



$$\underset{\underset{Br-Br}{\downarrow}}{RCH=CHR'}$$

charge transfer complex

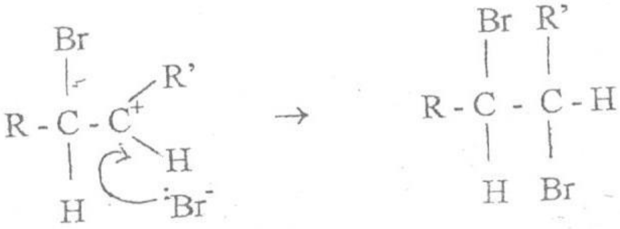
Thus the first step in the bromination of an alkene involves electrophilic attack on the double bond and the breaking of the carbon - carbon double bond (π-bond) and bromine - bromine to give a carbonium ion and a bromide ion.



Electrophilic attack (addition of Br^+)

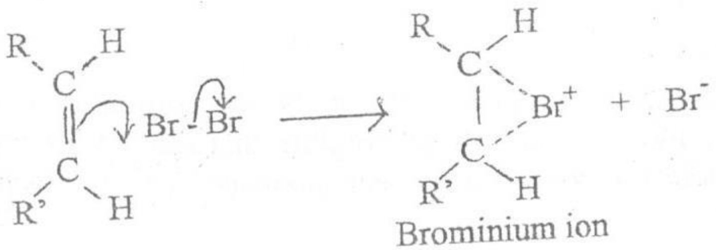
Carbonium ion

The second step is the rapid combination of the carbonium ion with the bromide ion.



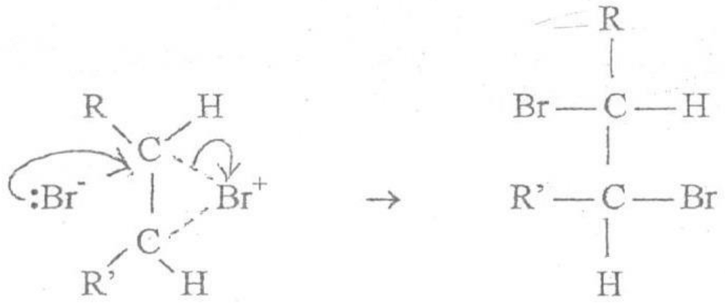
Nucleophilic attack (addition of Br^-)

The product of the addition reaction has been found to be the one in which the addition of the two bromine atoms takes place on the opposite sides of the alkene molecule (i.e. *trans*-addition). The simple mechanism outlined above does not account for this observation. To explain it, it has been suggested that the first bromine atom that adds to the alkene double bond is attached to both carbon atoms of the double bond to form a three-membered ring cyclic intermediate.



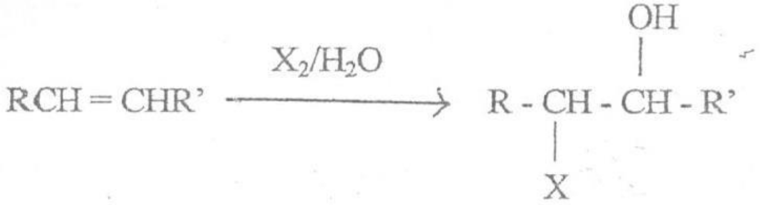
Brominium ion

The 'bridged' ion is called brominiun ion because bromine formally carries the positive charge. The bromide ion (nucleophile) then attacks one of the carbon atom from the side opposite the bridge and the ring opens.

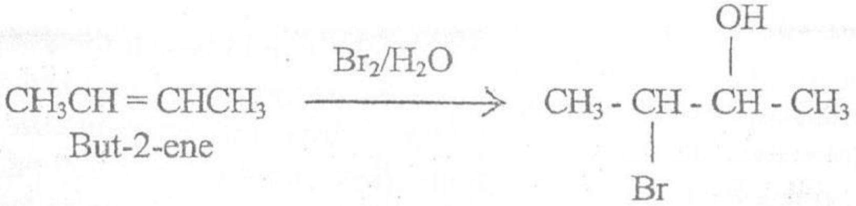


Addition of bromine or chlorine in aqueous solution (bromine water)

If bromination or chlorination is carried out in aqueous solution instead of tetrachloromethane, the major product is not a dibromo compound or dichloro compound but a bromoalcohol or a chloroalcohol.



$$RCH = CHR' \xrightarrow{X_2/H_2O} R - \underset{X}{CH} - \overset{OH}{CH} - R'$$



$$CH_3CH = CHCH_3 \xrightarrow{Br_2/H_2O} CH_3 - \underset{Br}{CH} - \overset{OH}{CH} - CH_3$$

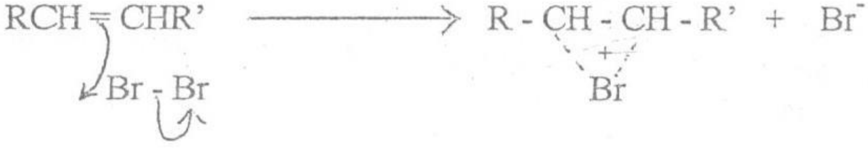
But-2-ene

3-Bromobutan-2-ol

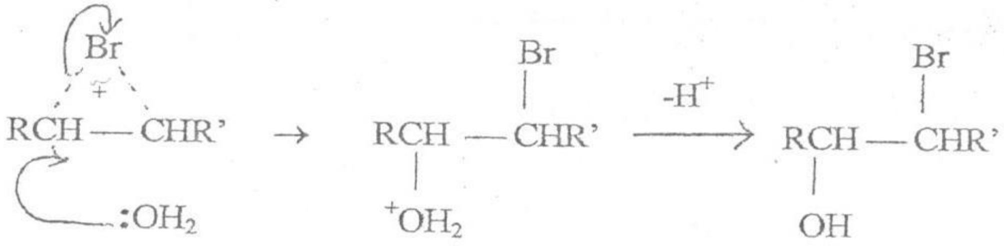
Chlorine reacts by similar mechanism.

Mechanism

The first step of the mechanism for the reaction leading to the formation of the bromoalcohol is the same as that for the addition of bromine in tetrachloromethane solution. It involves electrophilic addition of bromine to the alkene double bond to form a carbonium ion and a bromide ion.

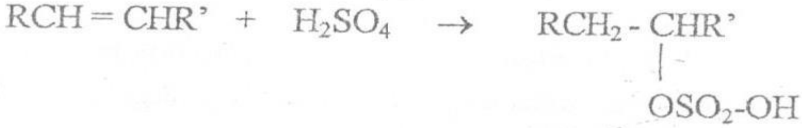


In the second step, water acts as the nucleophile using the lone pair of electrons on the oxygen atom. It is water that adds instead of the bromide ions because water is in excess compared to the bromide ions.



Addition of water in the presence of a mineral acid

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphate.



$$RCH = CHR' + H_2SO_4 \rightarrow RCH_2 - \underset{OSO_2\text{-}OH}{CHR'}$$

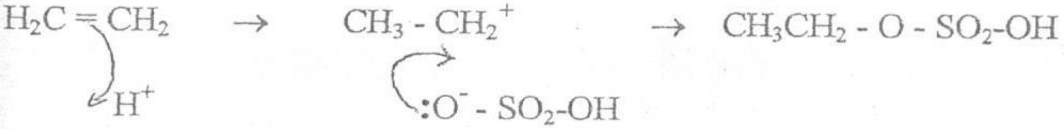
Alkyl hydrogen sulphate

$$H_2C = CH_2 + H_2SO_4 \rightarrow CH_3CH_2 - O - SO_2\text{-}OH$$

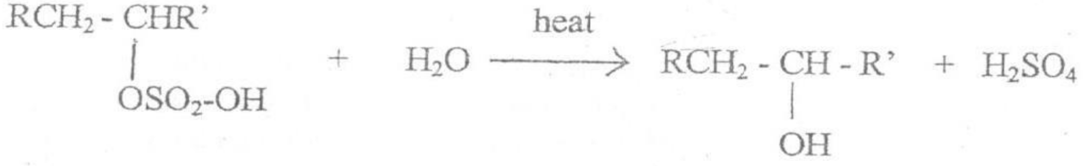
Ethyl hydrogen sulphate

Mechanism

The first step of the reaction is the addition of a proton to the double bond to form a carbonium ion. This is then followed by the nucleophilic addition of the hydrogen sulphate ion.



The alkyl hydrogen sulphate produced reacts with water to form an alcohol and sulphuric acid



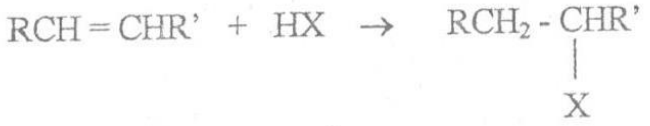
$$\underset{OSO_2\text{-}OH}{RCH_2 - CHR'} + H_2O \xrightarrow{heat} RCH_2 - \underset{OH}{CH} - R' + H_2SO_4$$

$$CH_3CH_2 - O - SO_2\text{-}OH + H_2O \xrightarrow{heat} CH_3CH_2OH + H_2SO_4$$

The reaction is used industrially in the manufacture of alcohols from alkenes.

Addition of hydrogen halide

Hydrogen halides react with alkenes to form alkyl halides.



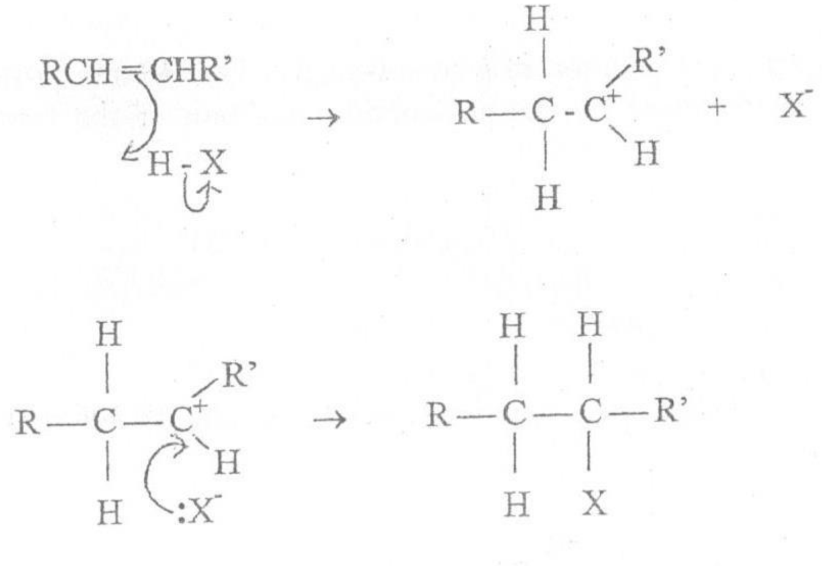
$$RCH = CHR' \; + \; HX \; \rightarrow \; RCH_2 - \underset{\displaystyle X}{\underset{|}{C}}HR'$$

(X = chlorine, bromine or iodine)

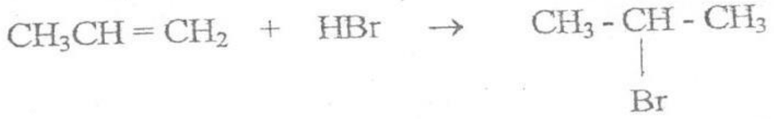
$$H_2C = CH_2 \; + \; HBr \; \rightarrow \; CH_3 - CH_2Br$$

Mechanism

The bond between hydrogen and the halogen atom is polar with the hydrogen atom being slightly positively charged and the halogen atom slightly negatively charged. The initial reaction is therefore is the addition of the hydrogen with the cleavage of the hydrogen - halogen bond to give a carbonium ion and an halide ion. This is then followed by the addition of the halide ion to the carbonium ion.



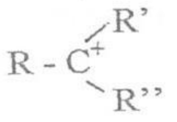
It has been observed that during the reaction the halogen atom adds to the less hydrogenated carbon of the double bond. The observation was first made by Markownikoff. It is therefore known as Markownikoff's rule, which states that when an acid HX adds to the double bond of an alkene, the hydrogen atom adds to the carbon atom of the double bond which has the larger number of hydrogen atoms.



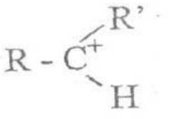
$$CH_3CH = CH_2 \;+\; HBr \;\rightarrow\; CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$$

The observation can be explained in terms of the stability of the intermediate carbonium ions formed during the reaction. The stability of carbonium ions is in the order Tertiary > Secondary > Primary > H_3C^+.

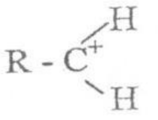
A tertiary carbonium ion is the one in which one in which the carbon atom bearing the positive charge is attached to three alkyl groups and a secondary carbonium ion is the one in which the positively charged carbon is bonded to two alkyl groups and a hydrogen. In a primary carbonium ion, the positively charged carbon atom is bonded to an alkyl group and two hydrogen atoms.



Tertiary carbonium ion

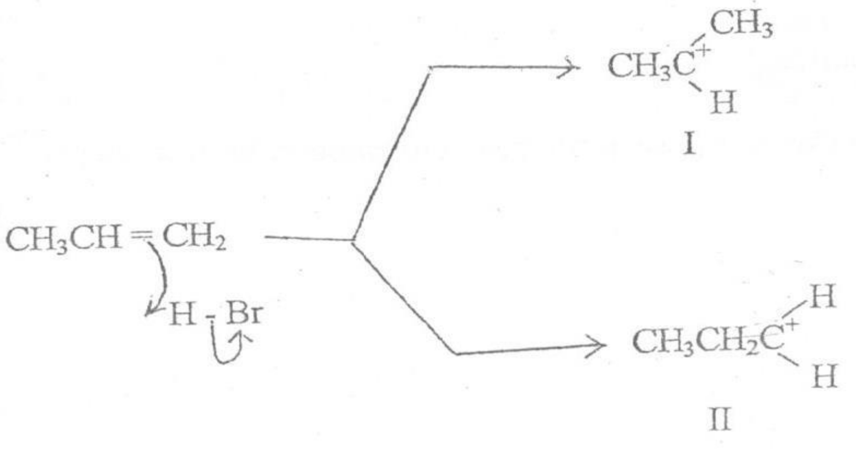


Secondary carbonium ion

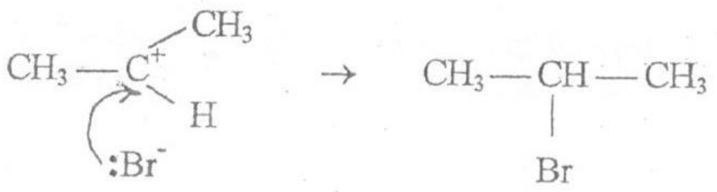


Primary carbonium ion

Consider the addition of hydrogen bromide to propene. The initial step ot the reaction is the addition of a proton. This can produce two possible carbonium ions



The carbonium ion (I) is a secondary carbonium ion while (II) is a primary carbonium ion. Thus, (I) will be the major intermediate since it is thermodynamically more stable than (II). The major intermediate will then react with the bromide ion (nucleophile) to form the observed product as the major product.



Addition of hydrogen bromide in the presence of a peroxide

In the presence of a peroxide (organic or inorganic), hydrogen bromide adds to alkenes to form a product that is different from the one predicted by Markownikoff's rule. In this case hydrogen atom adds to the carbon atom of the double bond that contains fewer hydrogen atoms.

$$RCH=CH_2 \quad + \quad HBr \xrightarrow{\text{peroxide}} RCH_2CH_2Br$$

$$CH_3CH=CH_2 \quad + \quad HBr \qquad \overset{\text{peroxide}}{} \qquad CH_3CH_2CH_2Br$$

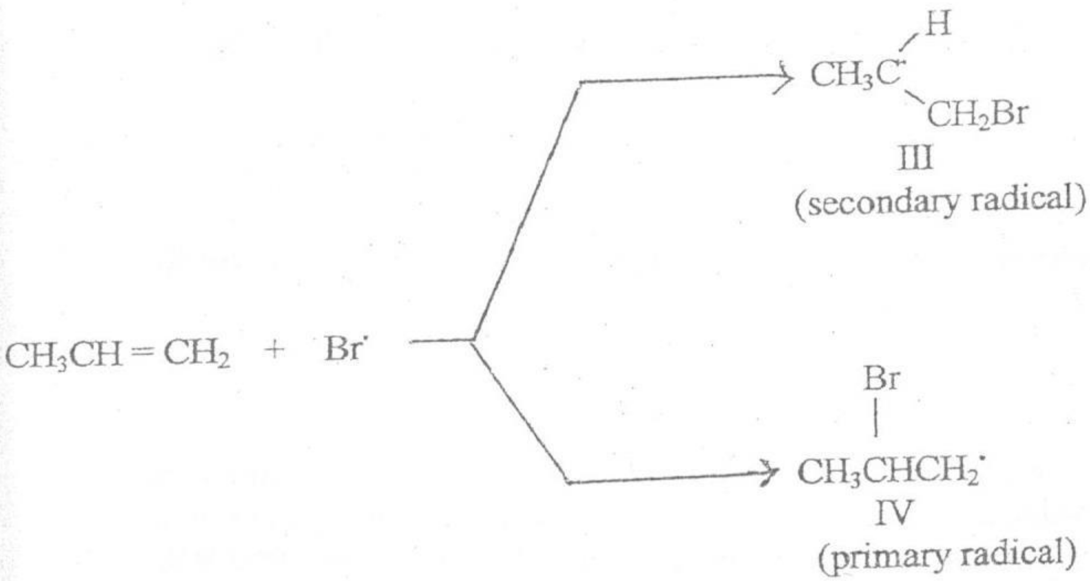
The explanation is that in the presence of a peroxide, the addition reaction follows a free radical rather than the ionic mechanism. The peroxide is decomposed by light or heat to free radicals.

$$\underset{\text{peroxide}}{RO - OR} \xrightarrow{h\nu} \underset{\text{free radicals}}{RO^{\cdot} \; + \; {}^{\cdot}OR}$$

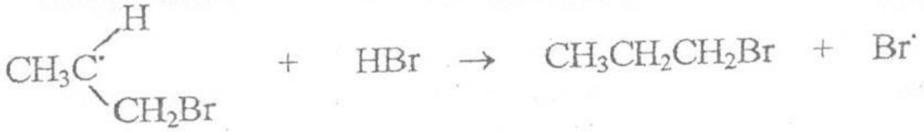
The radical from peroxide then reacts with hydrogen bromide molecule to form another radical.

$$RO. \quad + \quad HBr \quad \rightarrow \quad ROH \; + \; Br^{\cdot}$$

The bromide radical adds to the alkene double bond to form another radical



Since the stability of radicals are in the order tertiary > secondary > primary, the secondary radical (III) will be formed as the major intermediate in preference to the primary radical (IV). The secondary radical then reacts with another molecule of hydrogen bromide to give the observed product and a bromide radical that continues the chain reaction.



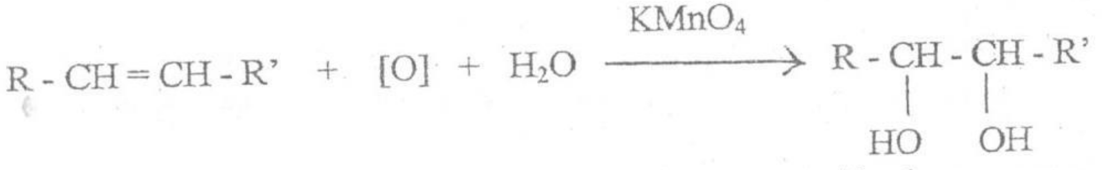
$$CH_3\dot{C}H(CH_2Br) + HBr \rightarrow CH_3CH_2CH_2Br + Br^{\cdot}$$

Oxidation of alkenes

Alkenes are readily oxidised by a number of reagents. Most of these reactions are used in synthesis, analysis and structural determination in organic chemistry.

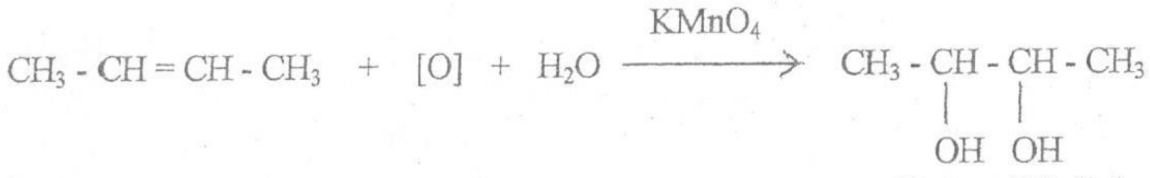
Reaction with potassium permanganate [potassium manganate(VII)] solution

Aqueous acid or alkaline potassium manganate(VII) is decolorised by alkene to form a dihydroxy compound.



$$R-CH=CH-R' + [O] + H_2O \xrightarrow{KMnO_4} R-CH(OH)-CH(OH)-R'$$

A dihydroxy compound



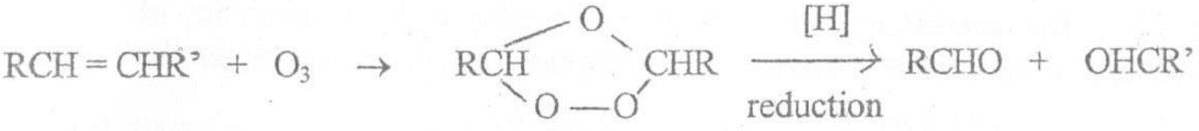
$$CH_3-CH=CH-CH_3 + [O] + H_2O \xrightarrow{KMnO_4} CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3$$

Butane-2,3-diol

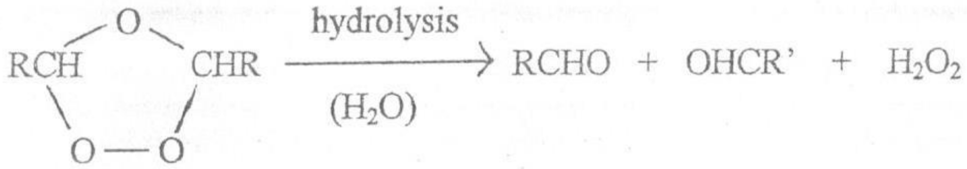
The decoloration of the permanganate in this reaction in this reaction is used as a test for the presence an alkene (carbon - carbon double bond).

Ozonized oxygen

When ozonized oxygen is passed through a solution of an alkene in trichloromethane at very low temperature, an ozonide is formed. Ozonides are unstable at high temperatures. They can explode even at room temperature. Ozonides can either be hydrolysed with water or reduced to give carbonyl compounds.



An ozonide



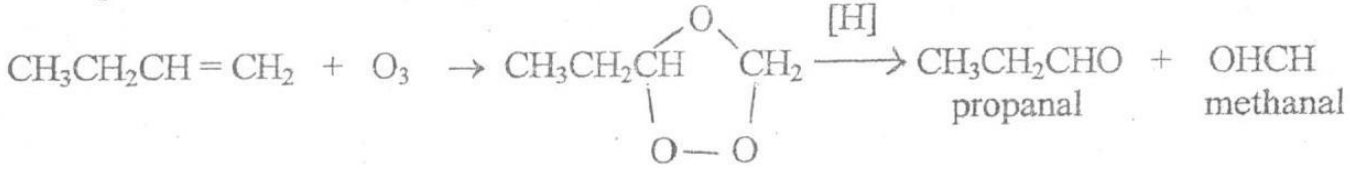
Some of the aldehyde formed is oxidised to carboxylic acid by the hydrogen peroxide.

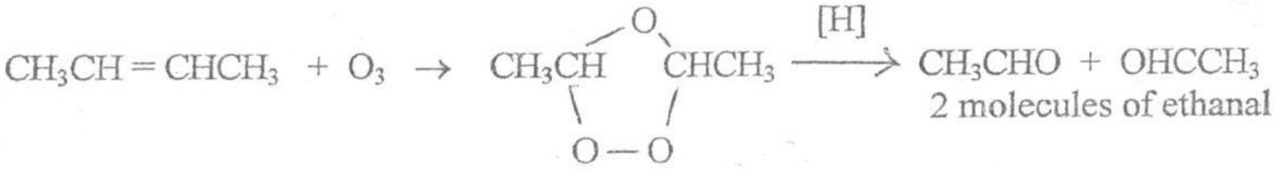
$$RCHO + R'CHO \xrightarrow{H_2O_2} RCO_2H + R'CO_2H$$

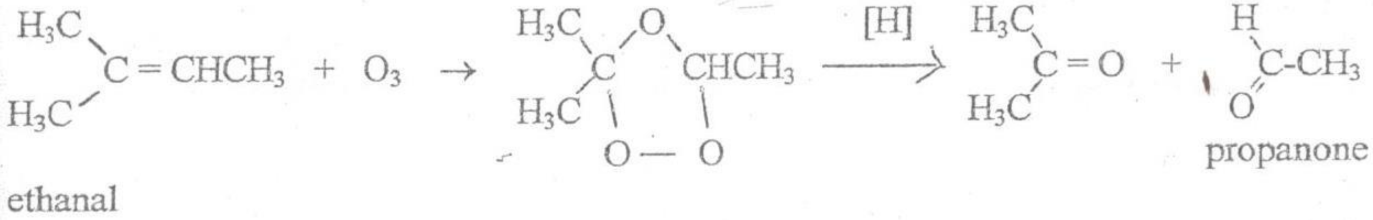
The whole process of reacting an alkene with ozinised oxygen followed by hydrolysis is known as ***ozonolysis***.

The reaction is of great importance in determining the position of the double bond in a molecule containing many carbon atoms. The ozonide on hydrolysis gives two carbonyl compounds, aldehydes or ketnes. An alkene with a terminal double bond gives methanal, an alkene with the structure RCH = gives an aldehyde and that with the structure RR'C = will give a ketone. An alkene with symmetrical double bond will give two identical aldehydes or ketone.

Examples


CH3CH2CH = CH2 + O3 →
CH3CH2CH O CH2 O — O
[H]
CH3CH2CHO + OHCH
propanal
methanal


CH3CH = CHCH3 + O3 →
CH3CH O CHCH3 O — O
[H]
CH3CHO + OHCCH3
2 molecules of ethanal


H3C C = CHCH3 H3C + O3 →
H3C O C CHCH3 H3C O — O
[H]
H3C C = O H3C
+
H C-CH3 O
propanone
ethanal

CHAPTER 4

ALKYNES (ACETYLENES)

Introduction

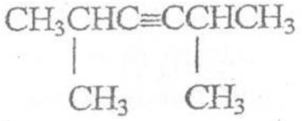
Alkynes are hydrocarbons containing a triple bond between two carbon atoms. They can be represented by the general formula $C_nH_{(2n-2)}$ or $RC \equiv CH$ or $RC \equiv CR'$.

Nomenclature

The rules for naming alkynes are the same as for alkenes except that the ending ***yne*** is used instead of *ene* for the alkenes.

(a) Substitute ***-yne*** for the ***-ane*** in the name of the corresponding alkane.
(b) The numbering in the branched chain alkynes is identical to that of alkene

Examples:

$HC\equiv CH$	ethyne or acetylene
$CH_3C\equiv CH$	propyne
$CH_3CH_2C\equiv CH$	but-1-yne
$CH_3C\equiv CCH_3$	but-2-yne
$CH_3CH_2C\equiv CCH_3$	pent-2-yne
$CH_3CH_2C\equiv CCH_2CH_3$	hex-3-yne
 $CH_3\underset{\substack{\vert \\ CH_3}}{CH}C\equiv C\underset{\substack{\vert \\ CH_3}}{CH}CH_3$	2,5-dimethylhex-3-yne

Physical properties

The physical properties of alkynes are similar to those of alkanes and alkenes. However, alkynes boil at higher temperatures than alkenes and alkanes with the same number of carbon atoms.

Physical constants of some alkynes

Formula	*Name*	*Mp (°C)*	*Bp (°C)*	*Density*
$HC \equiv CH$	Ethyne	-82	-83	-
$CH_3C\equiv CH$	Propyne	-101.5	-23.2	-
$CH_3CH_2C\equiv CH$	But-1-yne	-125.7	8.1	-
$CH_3C\equiv CCH_3$	But-2-yne	-32.3	27	0.691
$CH_3(CH_2)_2C\equiv CH$	Pent-1-yne	-90	39.3	0.695
$CH_3CH_2C\equiv CCH_3$	Pent-2-yne	-101	55.5	0.714

Industrial preparation of ethyne

(1) On industrial scale, ethyne is prepared by treating calcium(II) dicarbide (calcium carbide) with water. Calcium carbide itself is obtained by heating a mixture of calcium oxide (quicklime) and coke at 200 °C in an electric furnace.

$$\underset{\text{Quicklime}}{CaO} + 3C \xrightarrow{2000\ ^{\circ}C} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \rightarrow HC{\equiv}CH + Ca(OH)_2$$

(2) Ethyne can also be prepared by the partial combustion of methane.

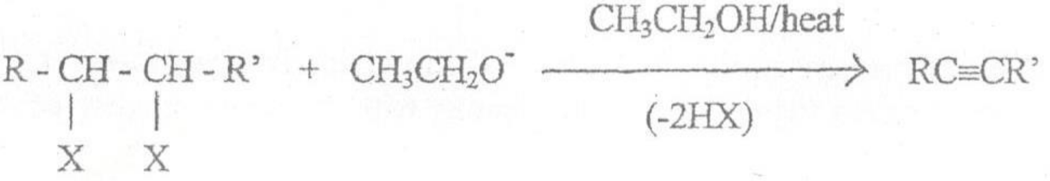
$$6CH_4 + O_2 \xrightarrow{1500\ ^{\circ}C} 2HC{\equiv}CH + CO + 4H_2O$$

Ethyne is separated from the mixture by passing the gases through a solvent like propanone or ammonia which absorbs it.

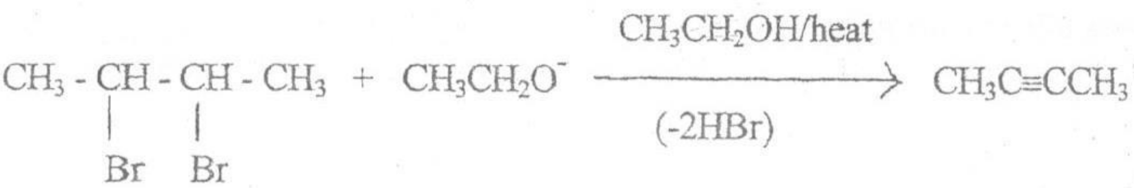
Laboratory synthesis of alkynes

Dehdrohalogenation of dihalogen compounds

Alkynes are obtained when a dihalogen compound is heated with a strong base [sodium ethoxide in ethanol or sodium amide in liquid ammonia (solution of sodium in liquid ammonia) or potassium hydroxide in ethanol (contains the ethoxide but not aqueous potassium hydroxide or alcoholic or aqueous sodium hydroxide)].



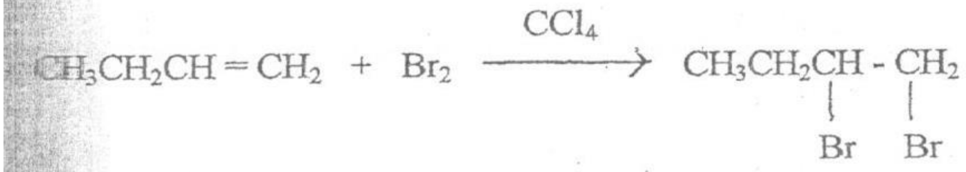
$$R-\underset{\underset{X}{|}}{CH}-\underset{\underset{X}{|}}{CH}-R' + CH_3CH_2O^- \xrightarrow[(-2HX)]{CH_3CH_2OH/heat} RC{\equiv}CR'$$



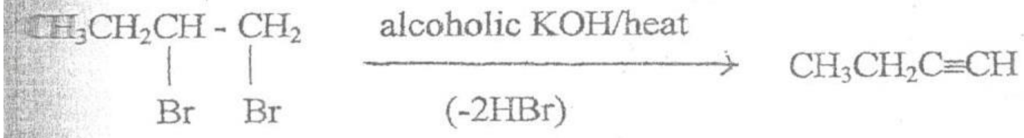
$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3 + CH_3CH_2O^- \xrightarrow[(-2HBr)]{CH_3CH_2OH/heat} CH_3C{\equiv}CCH_3$$

Dihalogen compounds are easily obtained from

(a) alkenes:



$$CH_3CH_2CH=CH_2 + Br_2 \xrightarrow{CCl_4} CH_3CH_2\underset{Br}{CH}-\underset{Br}{CH_2}$$



$$CH_3CH_2\underset{Br}{CH}-\underset{Br}{CH_2} \xrightarrow[(-2HBr)]{\text{alcoholic KOH/heat}} CH_3CH_2C\equiv CH$$

(b) carbonyl compounds (aldehydes and ketones):

$$CH_3CH_2CHO + PCl_5 \rightarrow CH_3CH_2CHCl_2 \xrightarrow[(-2HBr)]{\text{alcoholic KOH/heat}} CH_3C\equiv CH$$

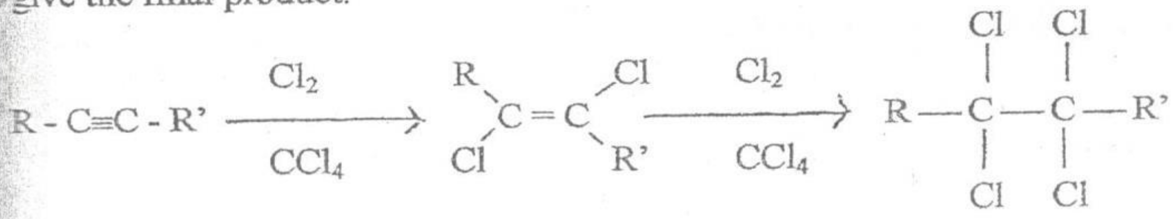
REACTIONS OF ALKYNES

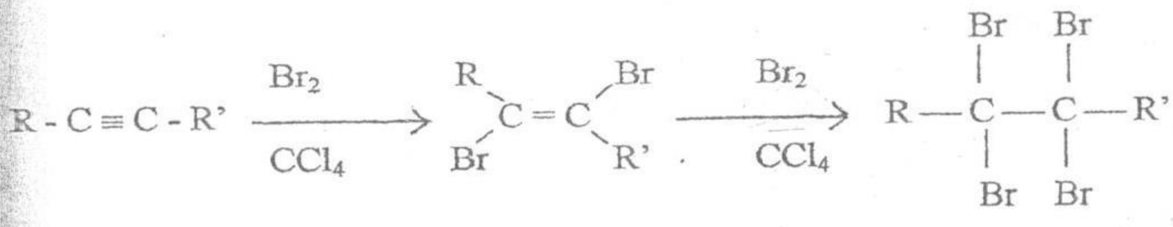
1. Electrophilic addition reactions

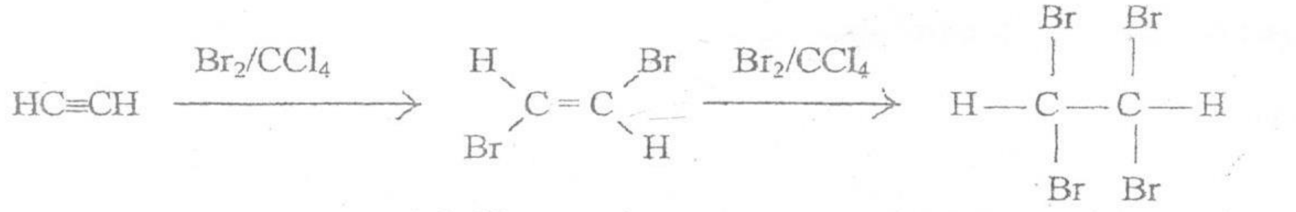
The carbon-carbon triple bond is less susceptible to electrophilic reaction than the carbon-carbon double. Nevertheless, alkynes undergo many addition reactions. The reactions are similar to those of alkenes but may take place in two stages

Addition of halogens

The addition of halogen to alkyne takes place in two stages to give a tetrahaloalkane. The first addition product is a dihaloalkene, which may add another molecule of the halogen to give the final product.





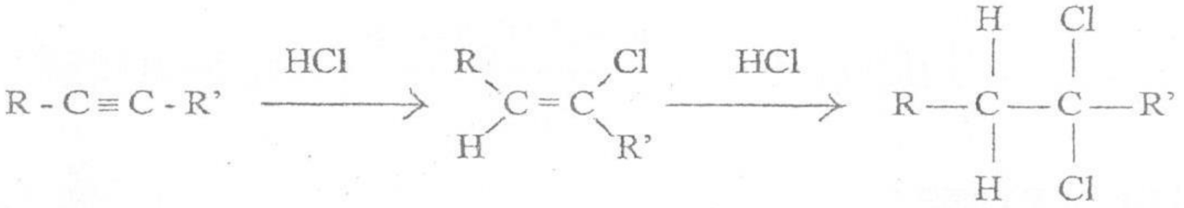


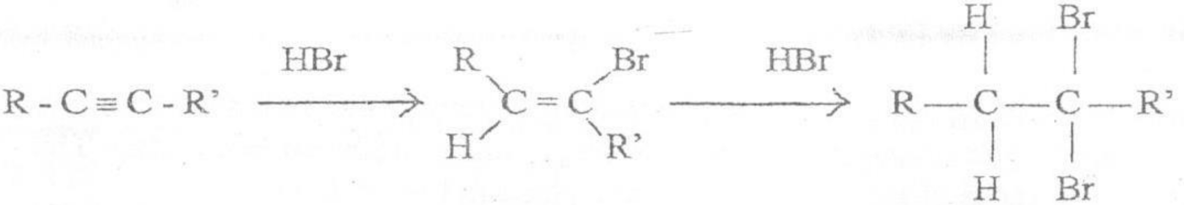
1,2-dibromoethene 1,1,2,2-tetraabromoethane

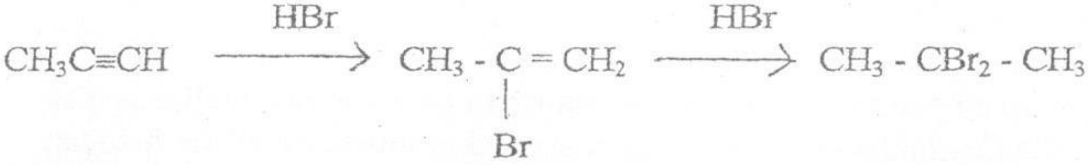
The dihaloalkene formed is less reactive than the triple bond. The reaction can thus be stopped at the haloalkene stage.

Addition of hydrogen halides

The reaction is similar to the addition of hydrogen halides to alkenes.







$$CH_3C\equiv CH \xrightarrow{HBr} CH_3 - \underset{\displaystyle Br}{\underset{|}{C}} = CH_2 \xrightarrow{HBr} CH_3 - CBr_2 - CH_3$$

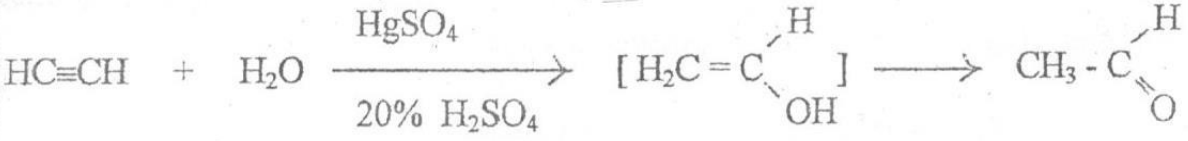
Addition of HBr in the presence of peroxides

$$CH_3CH_2CH_2CH_2C\equiv CH \xrightarrow[\text{peroxide}]{HBr} \underset{(74\%)}{CH_3CH_2CH_2CH_2CH = CHBr}$$

Addition of water (hydration)

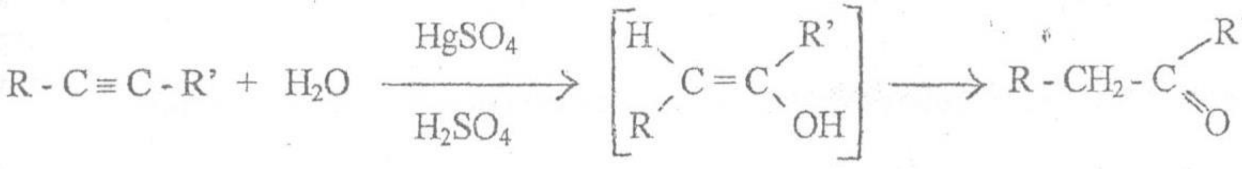
Alkynes add water readily. The reaction is catalysed b strong acids and mercury(II) ions. Aqueous sulphuric acid and mercury(II) sulphate are commonly used.

- Ethyne yield ethanal.
- Other alkynes give ketones.



$$HC\equiv CH + H_2O \xrightarrow[20\%\ H_2SO_4]{HgSO_4} [H_2C=C(H)(OH)] \longrightarrow CH_3-C(H)=O$$

The vinyl alcohol that is initially formed is unstable. It rearranges to ethanal.



$$R-C\equiv C-R' + H_2O \xrightarrow[H_2SO_4]{HgSO_4} \left[(H)(R)C=C(R')(OH)\right] \longrightarrow R-CH_2-C(R')=O$$

Replacement of the acetylenic hydrogen

(a) When an akyne with a terminal triple bond is passed into a solution of an alkali metal in liquid ammonia, a metal dicarbide (acetylide) is formed.

$$Na + NH_3 \xrightarrow{\text{Liq. } NH_3} \underset{\text{sodamide}}{Na^+NH_2^-} \xrightarrow{HC\equiv CH} \underset{\text{sodium acetylide}}{H\text{-}C\equiv C^-Na^+}$$

$$CH_3CH_2CH_2C\equiv CH + Na \xrightarrow{\text{liq. } NH_3} CH_3CH_2CH_2C\equiv C^-Na^+ + \frac{1}{2}H_2(g)$$

The terminal H of alkynes is therefore acidic.

The amide ion (anion of a weak acid, ammonia) removes the acetylenic protons of terminal alkynes.

Trend of basicity is:

NH_2^-	>	$RC\equiv C^-$	>	RCH_2O^-	>	HO^-
amide ion		acetylide ion		alkoxide ion		hydroxide ion

and the acid strength is in the order:

NH_3	<	$RC\equiv CH$	<	RCH_2OH	<	HOH
ammonia		ethyne		alcohol		water

Implication:

- Alkynes are more acidic than ammonia. Therefore sodium acetylide can be produced by reacting sodium amide with a terminal alkyne.

$$Na^+ NH_2 \; + \; RC\equiv CH \; \rightarrow \; RC\equiv C^- Na^+ \; + \; NH_3$$

- Reaction between acetylide (base) and water (acid) will produce an alkyne:

$$RC\equiv C^- Na^+ \; + \; H_2O \; \rightarrow \; RC\equiv CH \; + \; NaOH$$

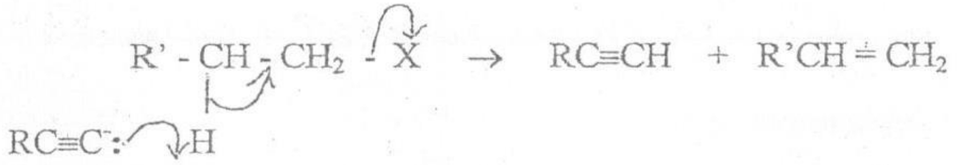
Acetylides are useful intermediates for the synthesis of acetylenic compounds.

1. *Synthesis of higher acetylenes*

$$RC\equiv CH \xrightarrow[2)\ RBr']{1)\ Na^+ NH_2} RC\equiv CR' \; + \; NaBr$$

R'Br should be primary.

Secondary and tertiary alkyl halides undergo elimination reactions since acetylides are strong bases.



$$R'-CH-CH_2-X \; \rightarrow \; RC\equiv CH \; + \; R'CH=CH_2$$

$$RC\equiv C^-\!:\;\;H$$

Other acetylides

$$RC\equiv CH \; + \; [Ag(NH_3)_2]^+ \; + \; {}^-OH \xrightarrow{H_2O} \underset{\substack{\text{silver}\\ \text{acetylide}\\ \text{(white)}}}{RC\equiv CAg} \; + \; H_2O \; + \; 2NH_3$$

$$RC\equiv CH \; + \; [Cu(NH_3)_2]^+ \; + \; {}^-OH \xrightarrow{H_2O} \underset{\substack{\text{copper}\\ \text{acetylide}\\ \text{(reddish-brown)}}}{RC\equiv CCu} \; + \; H_2O \; + \; 2NH_3$$

CHAPTER 5

AROMATIC HYDROCARBONS

BENZENE

Introduction

It was recognised for a long time that benzene and the compounds related to it possessed specific properties. For example, they had smell (aroma) which was different from other organic compounds. Hence they were given the name ***Aromatic*** compounds.

Although the aroma of these compounds were the least interesting property about them, chemists used the term aromaticity to describe the much important properties of benzene and compounds related to it, and called them aromatic compounds to distinguish them from aliphatic (open chain) compounds.

The structure of benzene

Elemental analysis and molecular mass determination gave the molecular formula of benzene as C_6H_6. A fully saturated compound would have a molecular formula of C_6H_{14}. Benzene therefore has eight hydrogen atoms less. If is aliphatic, it would have four double bonds, or two triple bonds or two double bonds and a triple bond. This means that benzene s a highly unsaturated compound.

However, benzene does not undergo typical addition reactions across the carbon-carbon double bond as alkenes. For example it does not

- react with hydrogen halides.
- add halogen atoms (e.g. bromine tetrachloromethane).
- add water in the presence of mineral acids.
- react with aqueous potassium permanganate.

The lack of reaction suggests that the double bonds in benzene are not typical double bonds found in alkenes and that benzene is unusually stable for such a highly unsaturated compound.

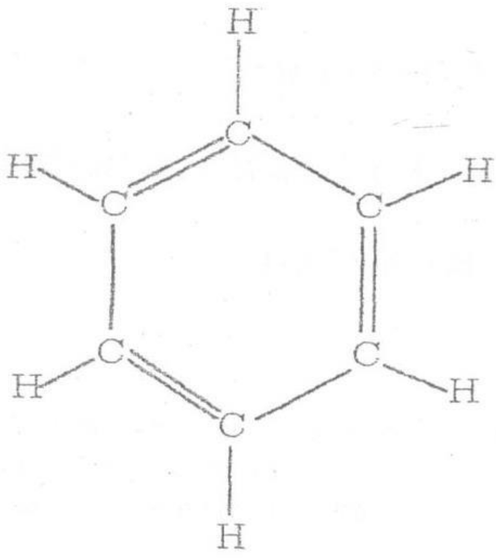
The Kekule structure of benzene

Kekule (1865) suggested that the carbon atoms of benzene are in a six-membered ring and that they are joined to each other by alternating single and double bonds, a hydrogen atom being bonded to each carbon atom.

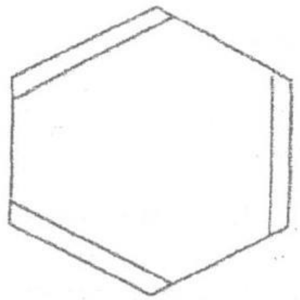
The two reactions above are used

- to distinguish between terminal acetylenes and internal acetylenes.
- in the separation of terminal alkynes.

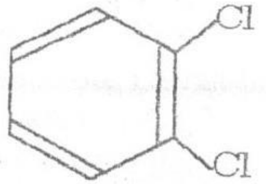
} Rxns of alkynes.



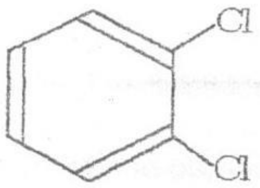
Or



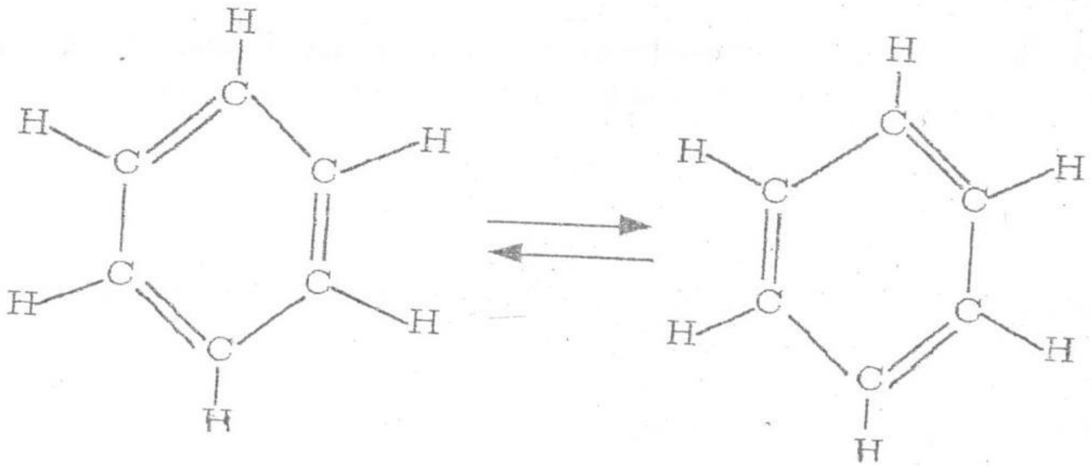
If this structure is correct, we would expect two isomers of 1,2-dichlorobenzene. One in which the two carbon atoms bonded to the chlorine atoms are separated by a double bond and the other in which they are separated by a single bond.



and



However, only one 1,2-dichlorobenzene is known. Kekule explained that the two forms of benzene (and derivatives of benzene) are in such a rapid state of equilibrium that it was not possible to isolate them.

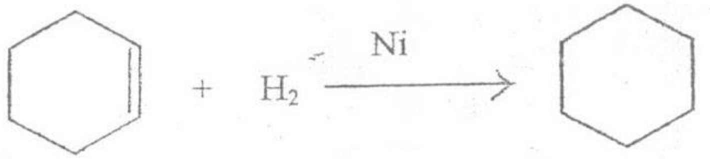


It is now known that Kekule's suggestion was wrong since such equilibrium does not exist. However it was an important step and is still used in practice today but with a different concept.

Stability of benzene

Benzene is more stable than the Kekule structure suggests and as mentioned above, it does not undergo addition reactions which would have been the case on the basis of Kekule structure. To illustrate that benzene is much more stable than expected, the enthalpy of its hydrogenation to cyclohexane was considered.

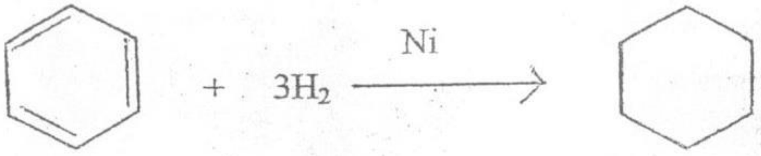
When cyclohexene, a six-membered ring alkene is hydrogenated to cyclohexane, the energy of the reaction is 119 $kJmol^{-1}$.



$\Delta H = -119\ kJmol^{-1}$

cyclohexene cyclohexane

If benzene were cyclohexa-1,3,5-triene, the heat liberated when it is hydrogenated to cyclohexane would be three times that liberated during the hydrogenation of cyclohexene. But when the experiment was carried out, it was found that only 207 $kJmol^{-1}$ of heat was liberated.



$\Delta H = -207\ kJmol^{-1}$

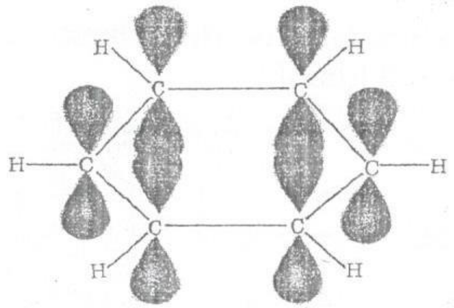
benzene cyclohexane

Calculated enthalpy of hydrogenation of benzene = 3 x 119 = 357 $kJmol^{-1}$
Experimental enthalpy of hydrogenation of benzene = $\underline{207}$ $kJmol^{-1}$
Difference = 150 $kJmol^{-1}$

The result shows that benzene is much more stable than cyclohexa-1,3,5-triene by 150 $kJmol^{-1}$ The difference between the calculated and the observed (experimental) enthalpy of hydrogenation is known as ***resonance or delocalisation*** energy.

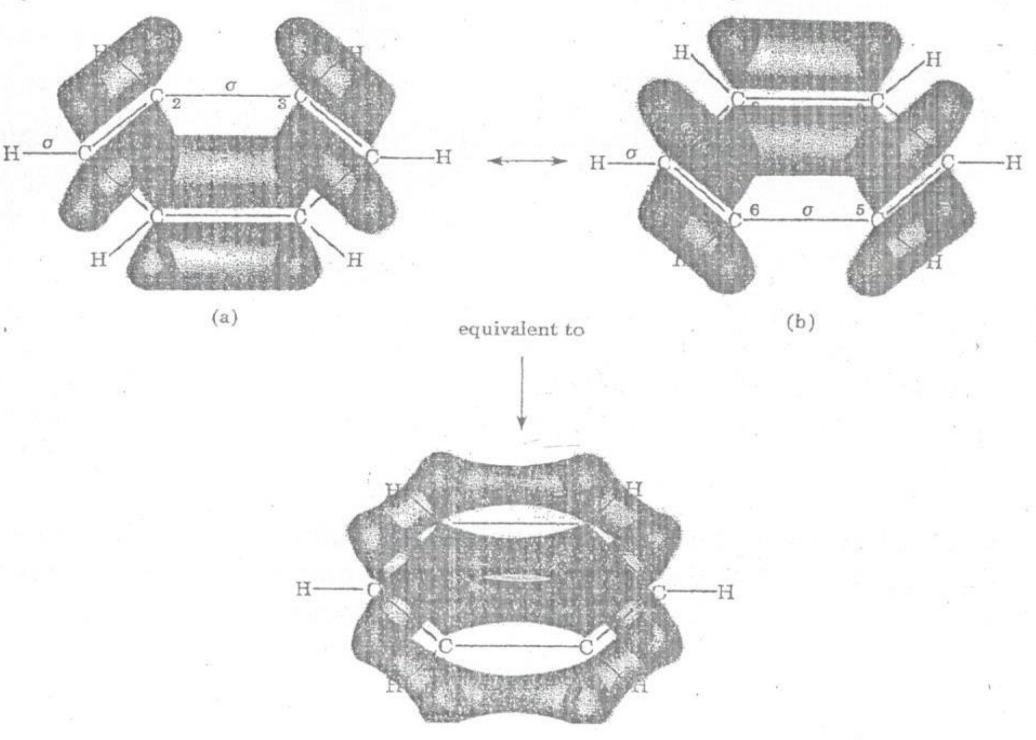
Molecular orbital treatment of the benzene molecule

It was known for a long time that benzene is a ring compound and that the C-C and the C-C-H bond angles in benzene are 120° thus suggesting that the carbon atoms in benzene are sp^2 hybridised and each hydrogen atom must be attached to the sp^2 hybridised carbon atom. Thus the six-membered ring of carbon atoms is formed (σ-bonds) and each carbon atom forms a bond with a hydrogen atom. Each carbon is thus left with a singly occupied p orbital.



Molecular orbital picture of benzene without *p* orbital overlap.

The carbon atoms are so close (1.39 A° apart), so each of the p orbital with the p orbital on either side thus forming a delocalised π molecular orbital which extends all around the ring. The delocalised orbital lies in a plane above and below the plane containing the carbon and hydrogen atoms and contains six electrons.

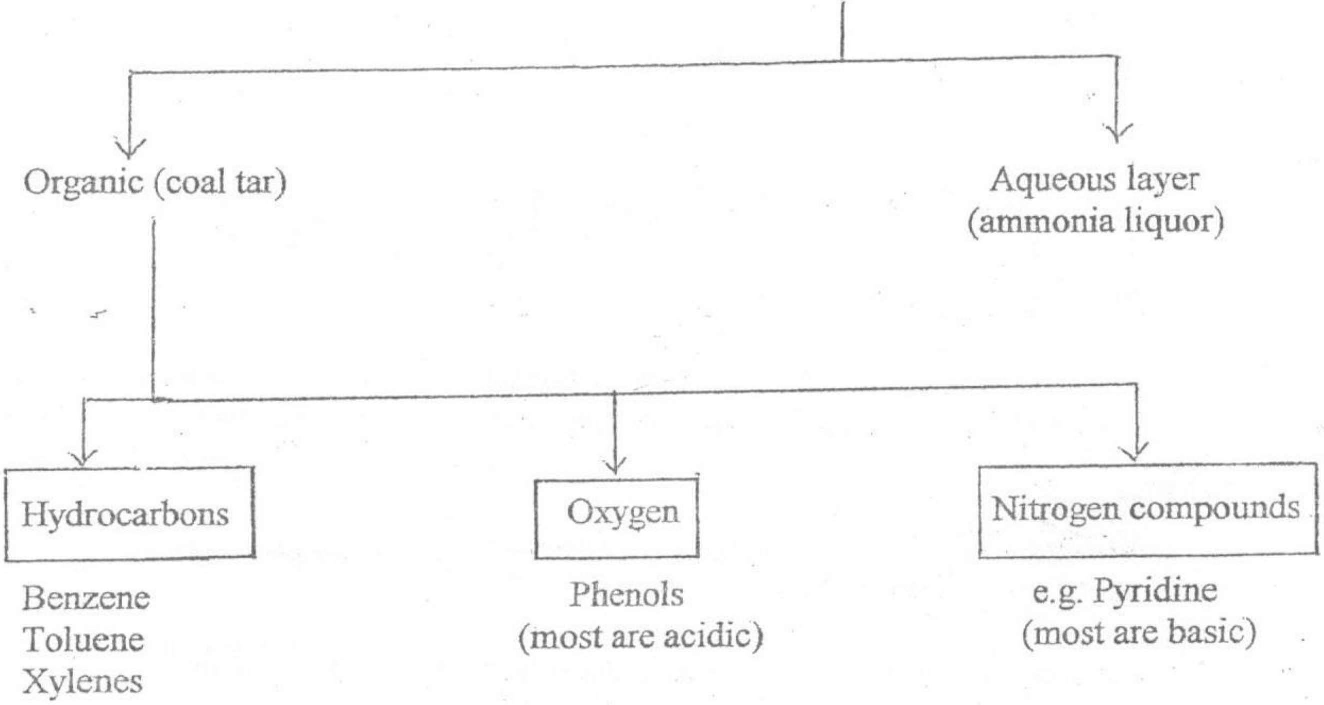


Source of benzene

(a) From coal tar

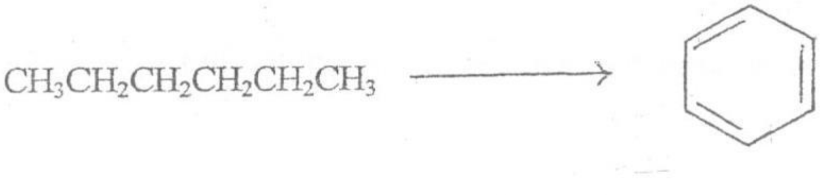
Benzene is obtained from coal tar by fractional distillation of coal tar.

$$\text{Coal tar} \xrightarrow{1000\ ^{\circ}\text{C}} \text{coke} + \text{coal gas} + \text{liquid products}$$



(b) From petroleum

(i) By catalytic cracking of larger and more saturated hydrocarbons. Metal oxides e.g. Cr_2O_3-Al_2O_3 are normally used as catalysts.
(ii) By catalytic reforming of lower petroleum fractions, under pressure at about 500 °C.

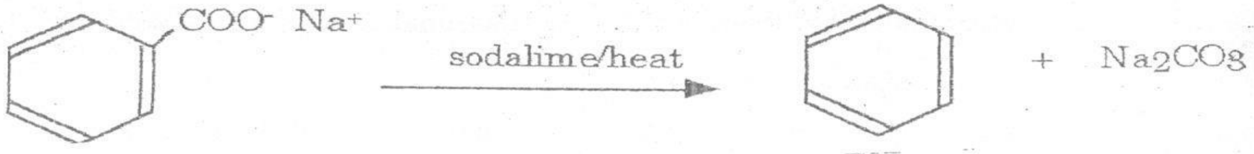


Laboratory preparation of benzene

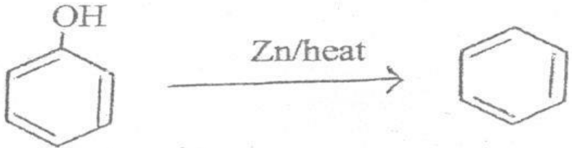
Benzene is normally not synthesised in the laboratory but may be prepared by the following methods.

Benzene is normally not synthesised in the laboratory but may be prepared by the following methods.

Decarboxylation of sodium benzoate



Reduction of phenol (hydroxybenzene)



Physical properties of benzene

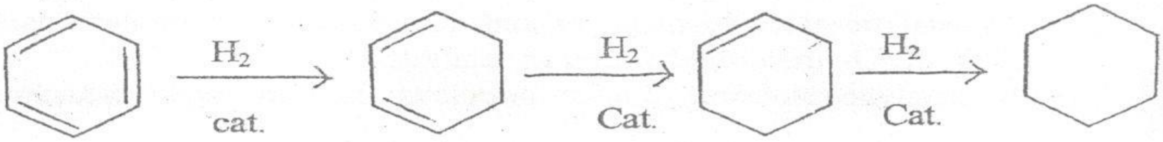
Benzene is a colourless liquid, with boiling point of 80 oC and freezes at 5 oC. It is insoluble in water but dissolves in organic solvents and is itself a good solvent.

Reactions of benzene

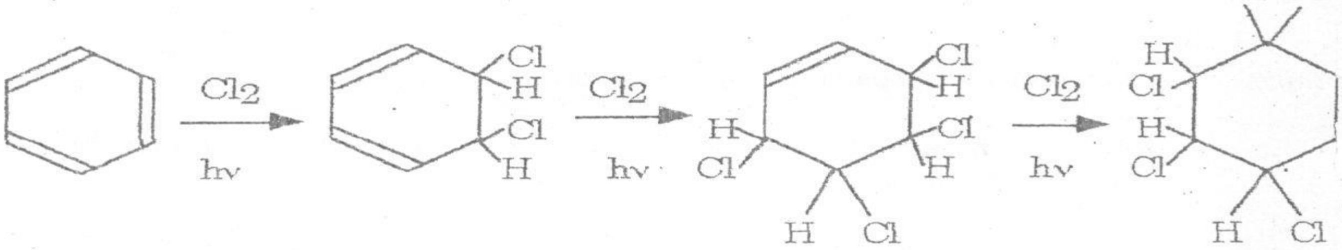
Addition reactions

Benzene undergoes few addition reactions under forcing conditions.

(i) The double bond of benzene can be catalytically hydrogenated at high temperatures and pressure.



(ii) Chlorine adds to benzene in the presence of sunlight or ultraviolet radiation.



1,2,3,4,5,6-hexacl
cyclohexane

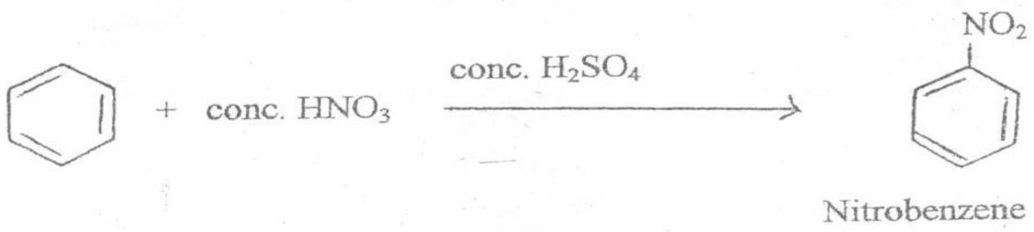
1,2,3,4,5,6-hexachloro-
cyclohexane.

Nucleophilic substitution reactions of benzene

Unlike alkenes, benzene undergoes a number of substitution reactions with electrophiles. In these reactions a hydrogen atom of the benzene is replaced by another atom or functional group. It is these reactions which distinguish benzene and other aromatic hydrocarbons from alkenes.

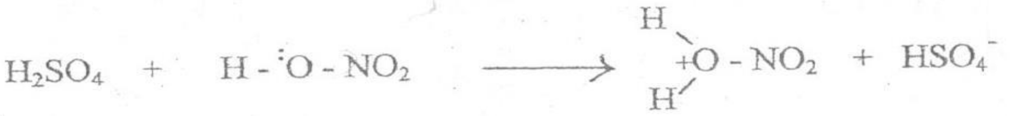
Nitration of benzene

When benzene is warmed with a mixture of concentrated nitric acid and concentrated sulphuric acid, nitrobenzene is formed.



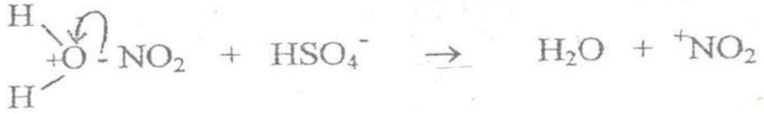
The purpose of sulphuric acid is to generate the electrophile, nitronium ion, +NO2, from nitric acid.

The first step of the reaction is the protonation of nitric acid by sulphuric acid (stronger acid).



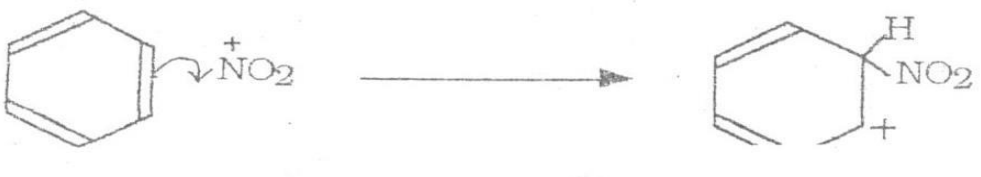
$$H_2SO_4 \quad + \quad H-\ddot{O}-NO_2 \longrightarrow \overset{H}{\underset{H}{\overset{\diagdown}{\underset{\diagup}{+O}}}}-NO_2 \quad + \quad HSO_4^-$$

The protonated nitric acid then undergoes heterolysis with elimination of a water molecule to give the nitronium ion.

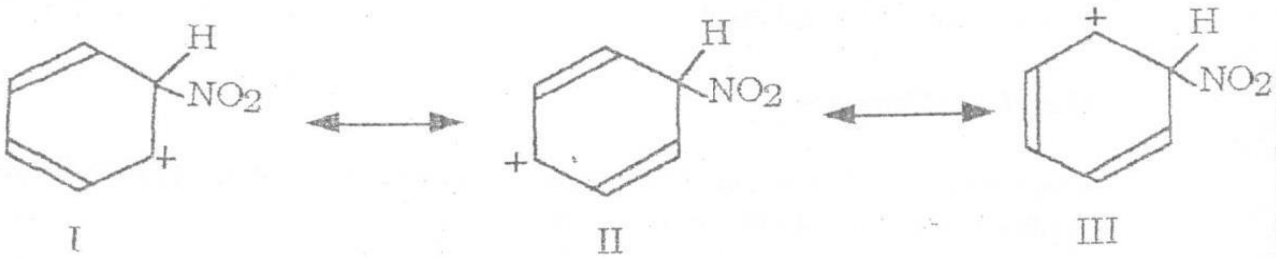


$$\overset{H}{\underset{H}{\overset{\diagdown}{\underset{\diagup}{+O}}}}-NO_2 \quad + \quad HSO_4^- \quad \rightarrow \quad H_2O \quad + \quad {}^+NO_2$$

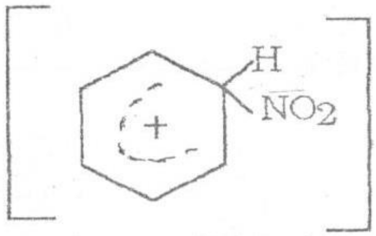
The nitronium ion then reacts with benzene to give a species in which the positive charge is delocalised over three carbon atoms of the benzene ring.



The above structure is represented as a resonance hybrid of the three structures, I , II and III below.



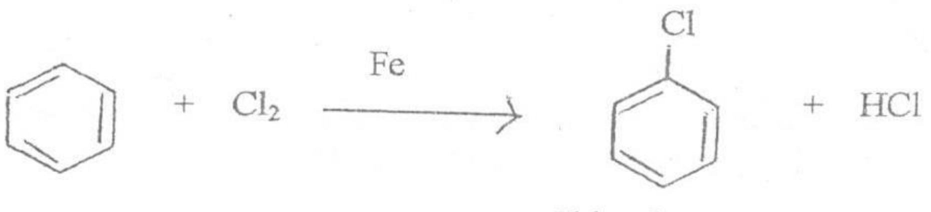
To indicate that the positive charge is delocalised, the species is normally written as below.



The final step is the removal of a proton from the species by the hydrogen sulphate ion.

Halogenation of benzene

When chlorine or bromine is passed through benzene at room temperature in the presence of a halogen carrier (e.g. iron filings, aluminium chloride or iodine), monochlorobenzene (or monobromobenzene) is formed.

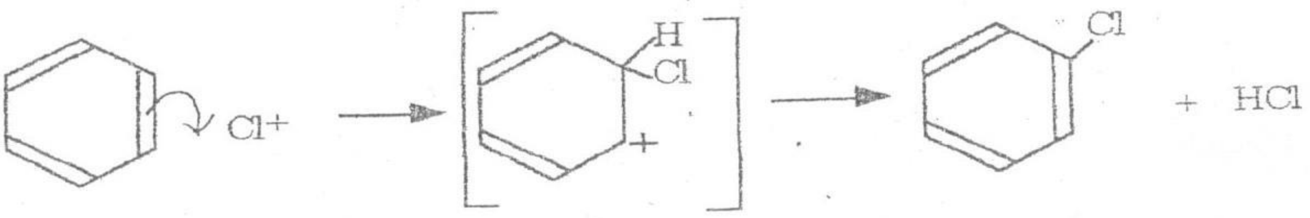


The role of the halogen carrier is to generate a more powerful electrophile. (Iron is first converted to iron(III) chloride by chlorine).

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

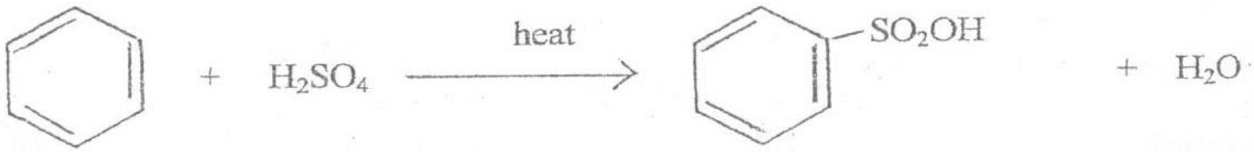
$$Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$$

or $$Cl_2 + FeCl_3 \rightarrow Cl^{\delta+} \ldots Cl^{\delta-} \ldots FeCl_3$$



Sulphonation of benzene

Benzenesulphonic acid is formed when a mixture of concentrated (or fuming) sulphuric acid is heated under reflux for 8 hours.

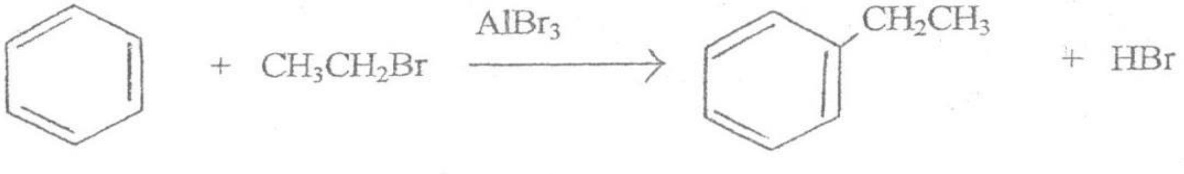


Benzenesulphonic acid

Friedel Crafts reaction

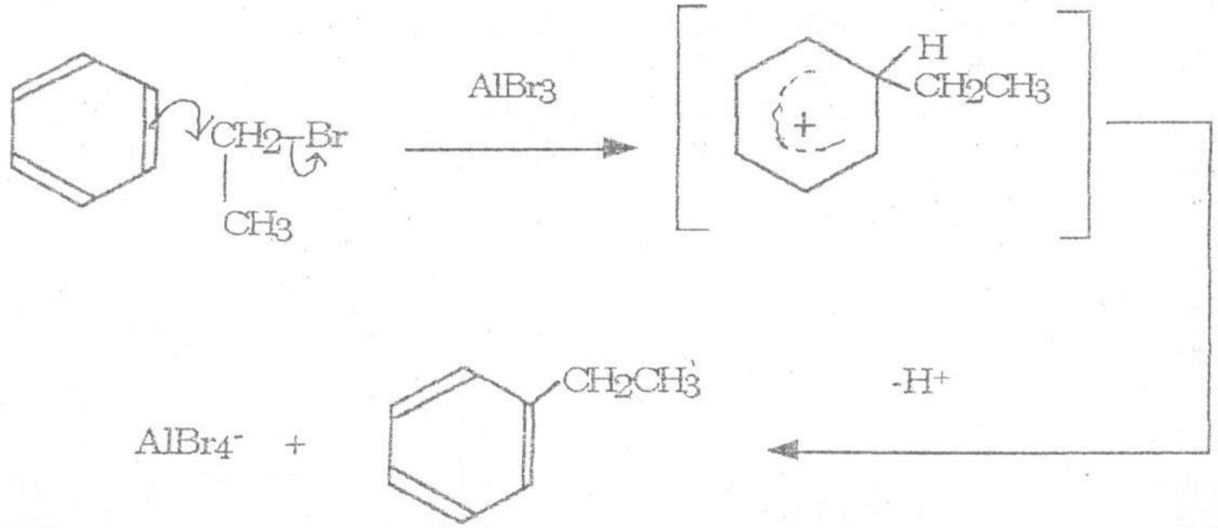
Alkylation

Benzene reacts with alkyl halides in the presence of a catalyst to form alkylbenzenes. The catalysts are normally Lewis acids, for example aluminium halides.

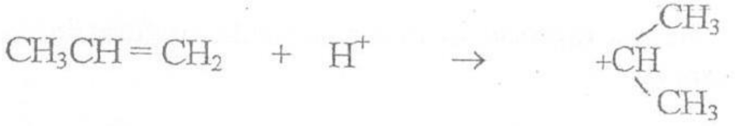


Ethylbenzene

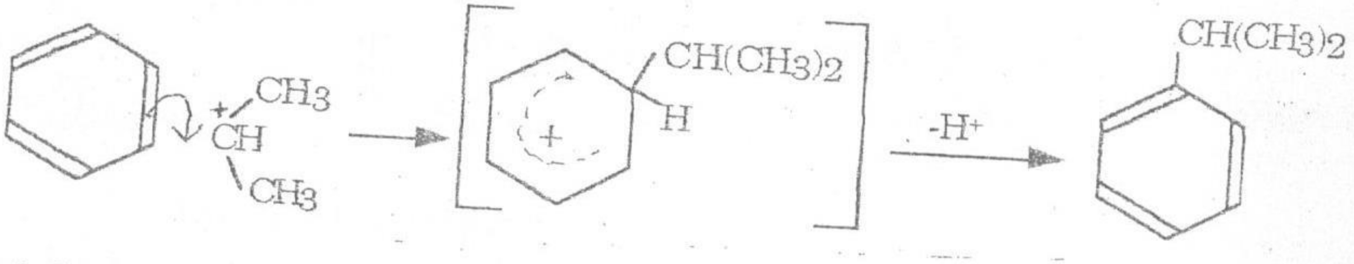
Mechanism



In the presence of acid, benzene reacts with alkenes to form alkylbenzenes. In this case the reaction proceeds through the formation of a carbonium ion.

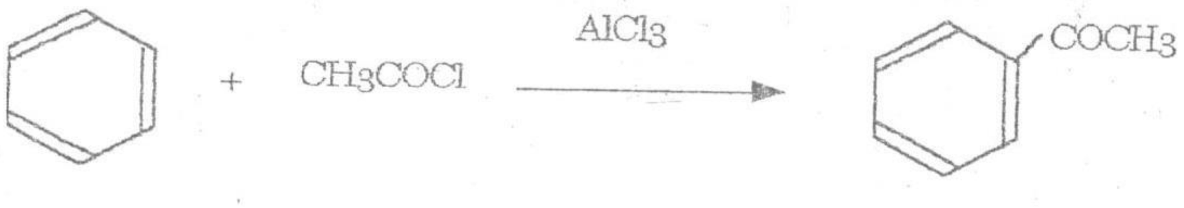


$$CH_3CH{=}CH_2 \quad + \quad H^+ \quad \rightarrow \quad {}^{+}CH(CH_3)_2$$



Acylation

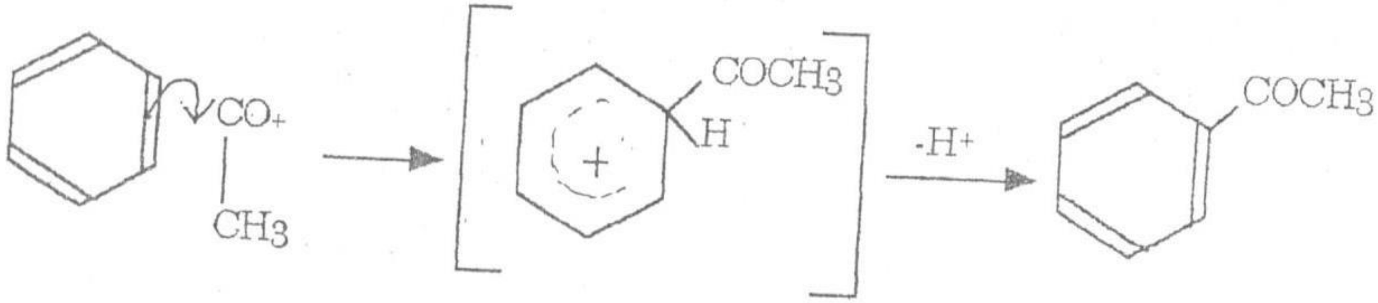
Acyl halides (acid halides), RCOCl, react with benzene in the presence of aluminium chloride to form aromatic ketones.



Acetophenone

Mechanism

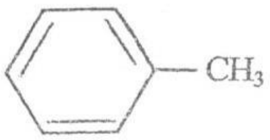
$CH_3COCl + AlCl_3 \rightarrow CH_3C{\equiv}O^+ + AlCl_4^-$



CHAPTER 6

TOLUENE (METHYLBENZENE)

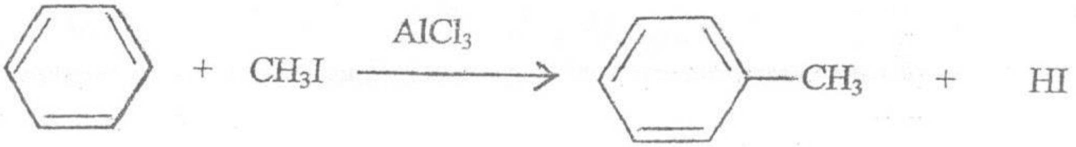
Structural formula



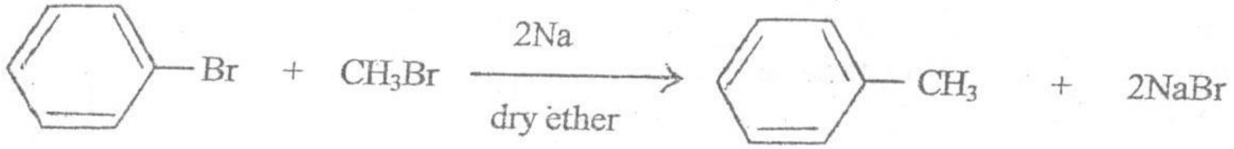
Source

Toluene is obtained from coal tar by fractional distillation of the 'light-oil' and by cracking of petroleum products.

In the laboratory, toluene can be prepared by Friedel Crafts reaction.



Toluene can also be prepared by Wurtz-Fittig reaction.



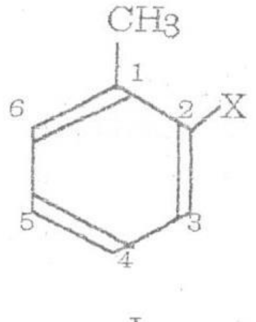
Physical properties of toluene

Toluene is a colourless liquid, boiling point 110° C and freezing point -95° C. It is insoluble in water but is soluble in organic solvents and is itself a good solvent.

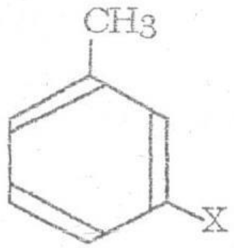
Reactions of toluene

Electrophilic substitution reactions

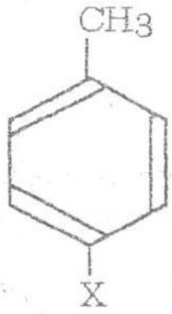
Toluene is attacked by the electrophilic reagents which react with benzene but is more reactive than the latter because of the methyl group attached to the ring. There are three possible isomeric products.



I



II



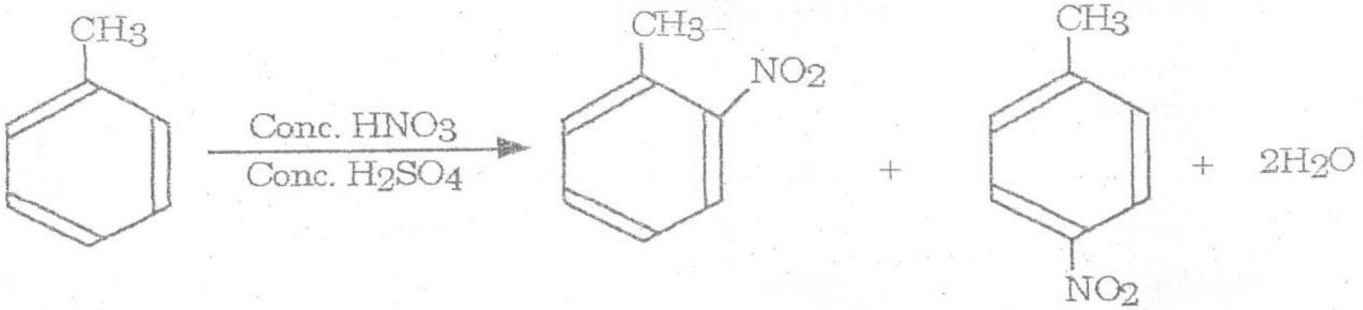
III

In (I) the substitution enters the 2-position (also known as the *ortho-* position and abbreviated *o-*). In (II) the substituent is in the 3-position (the *meta-* position, abbreviated *m*) and in (III) the substituent is in the 4-position (*para-* position, abbreviated *p-*). Position 2 is similar to position 6 and position 3 is similar to position 5.

The methyl group directs the incoming substituent to the 2- and 4-positions. Thus the *ortho-* and *para-*isomers are the major products of the substitution reactions of toluene.

Nitration of toluene

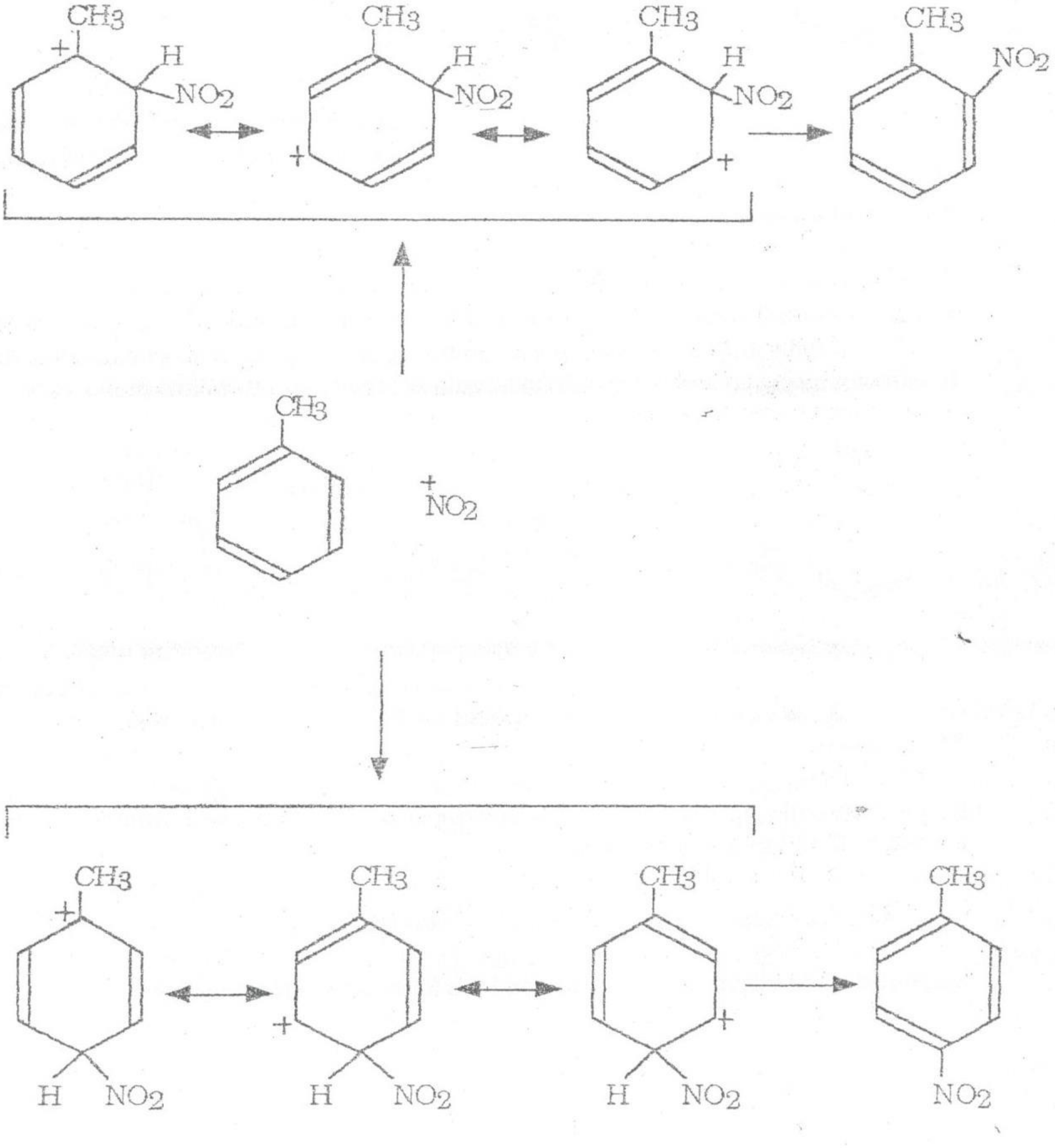
Toluene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form *para-*nitrobenzene and *ortho-*nitrobenzene. The mixture needs warming.



59%
o - Nitrotoluene

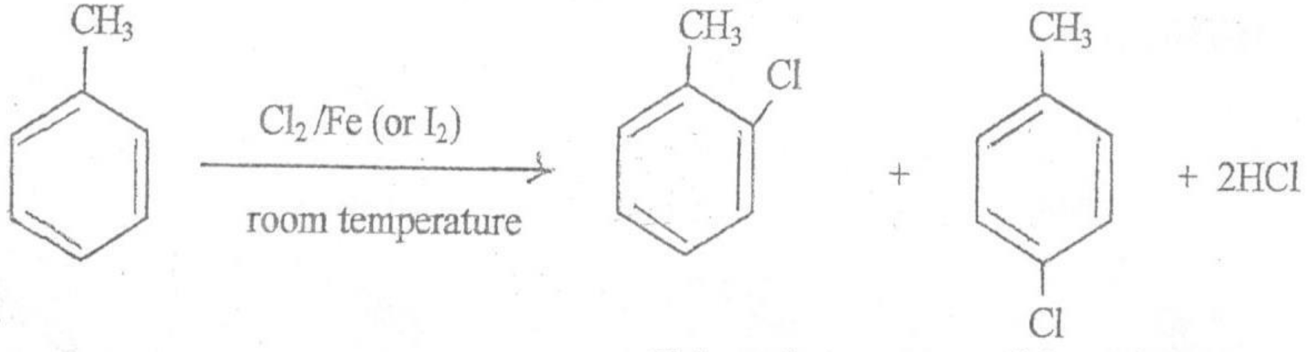
37%
p - Nitrotoluene

Mechanism



Halogenation of toluene

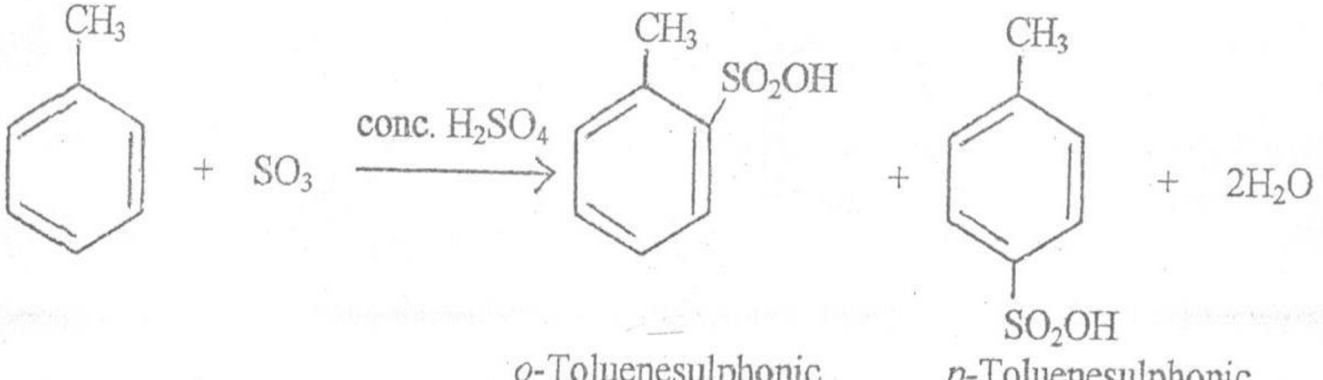
Toluene reacts with chlorine in the presence of a halogen carrier (e.g. iron or iodine) to form *ortho*-chlorobenzene and *para*-chlorobenzene.



o-Chlorotoluene (2-chlorobenzene) *p*-Chlorotoluene (4-chlorobenzene)

Sulphonation of toluene

Toluene reacts with fuming sulphuric acid at room temperature to form a mixture of *ortho*-toluenesulphonic *acid* and *para*-toluenesulphonic acid. Fuming sulphuric acid contains sulphur trioxide which appears to be the electrophile. The sulphonation can also be effected using concentrated sulphuric acid but the reaction is slow in this case.



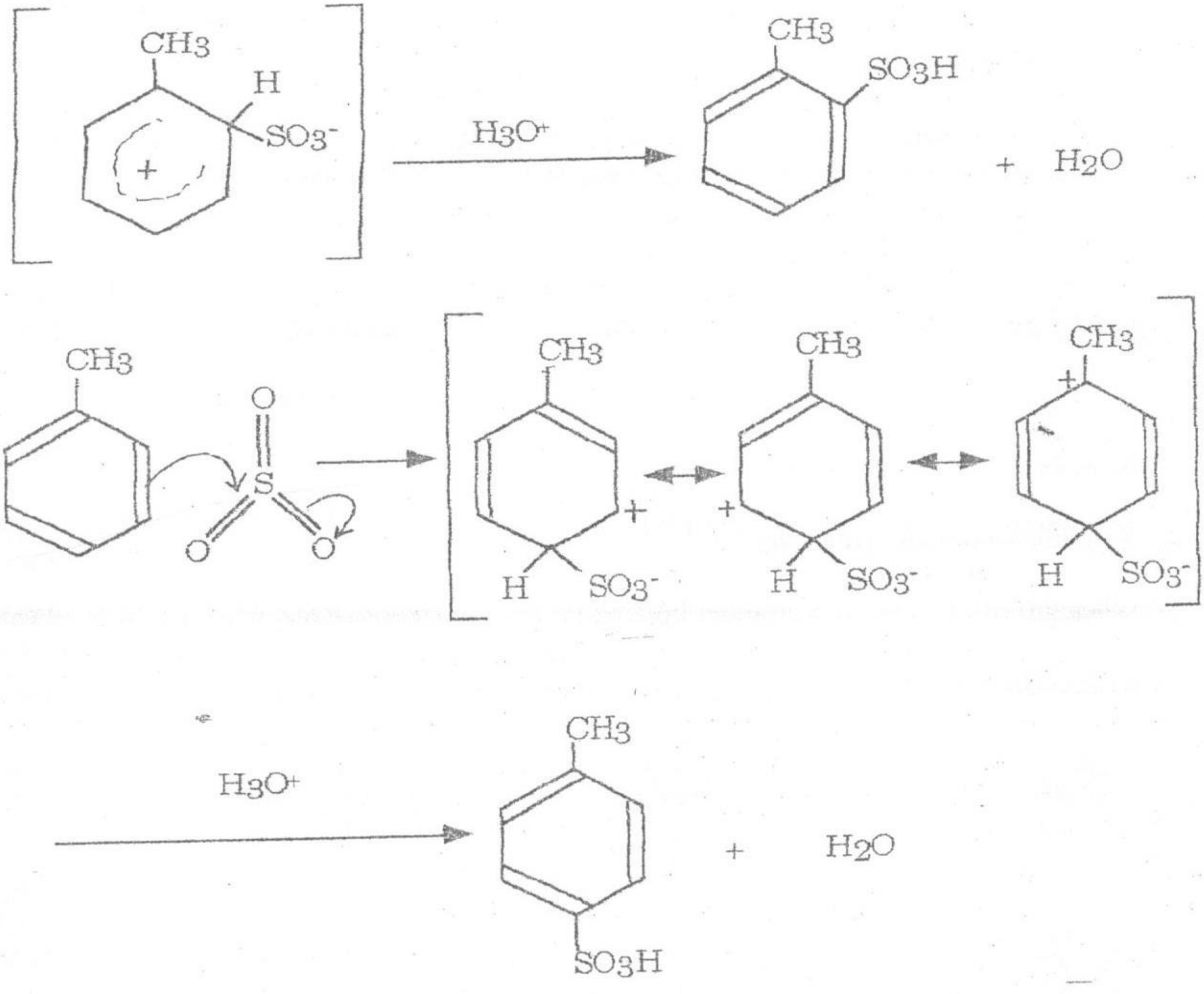
o-Toluenesulphonic acid *p*-Toluenesulphonic acid

Mechanism

Sulphur trioxide appears to be the electrophile. It is produced from sulphuric acid according to the following equation:

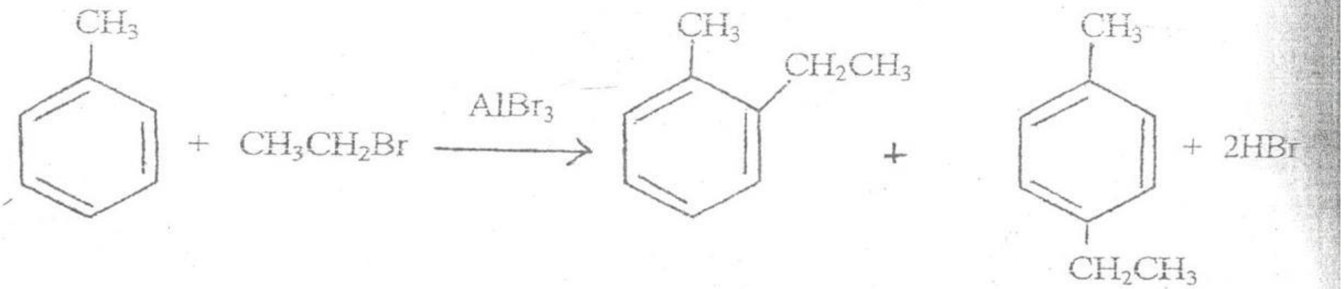
$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$$

Sulphuric acid behaves as both acid and base in the above reaction.



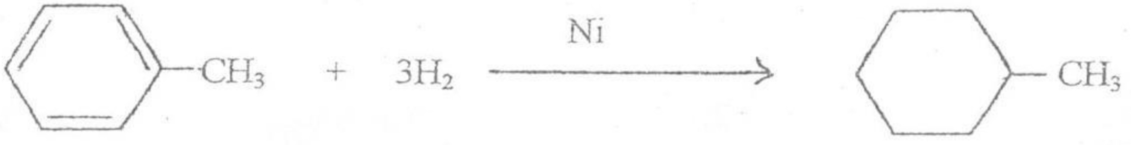
Alkylation

Toluene reacts with alkyl halides to form *ortho-* and *para-*alkyl derivatives. However, since toluene is more reactive towards electrophilic substitution reactions than benzene, polysubstition normally takes place.



Addition reaction

Addition reaction to the ring of toluene is similar to that of benzene. In the presence of nickel, toluene is reduced y hydrogen gas to methylcyclohexane.

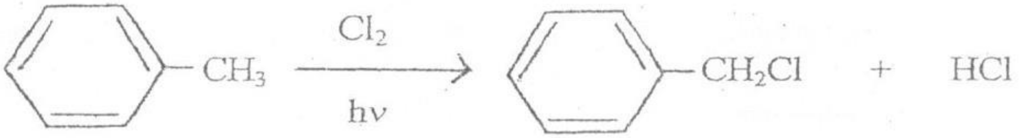


Methylcyclohexane

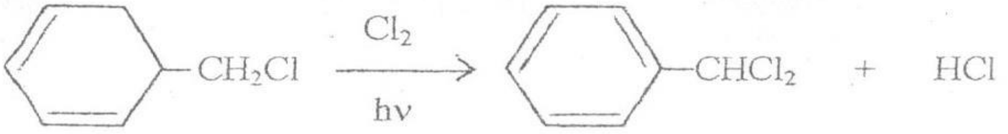
Reaction of the side chain

Substitution in the side chain

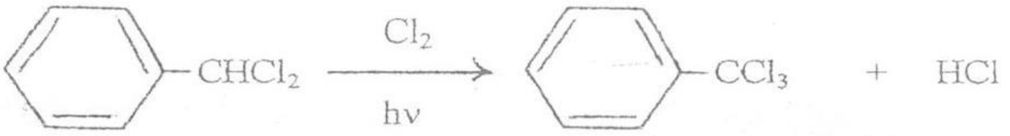
When chlorine is passed through boiling toluene in the presence of sunlight or ultraviolet radiation, chlorination of the side chain takes place, similar to the reaction of methane with chlorine.



Benzyl chloride



Benzal chloride

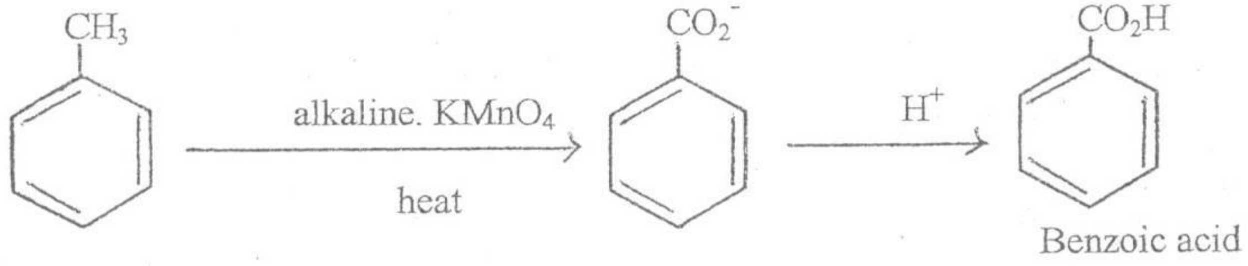


Benzotrichloride

The reaction is similar to the chlorination of methane and takes place by free radical mechanism as discussed for methane.

Oxidation of the side chain

The side chain of toluene is oxidised by hot alkaline potassium to carboxyl group, CO_2H



CHAPTER 7

HALOGEN COMPOUNDS

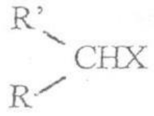
Introduction

Alkyl halides

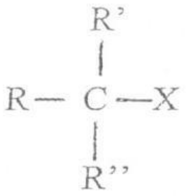
Alkyl halides are compounds in which the halogen atom is bonded to a saturated carbon atom. The halogens normally studied under this heading are chlorine, bromine and iodine because they are very useful in organic synthesis. Fluorine compounds are not included because the carbon - carbon bond is strong thus making alkyl fluorides unreactive. However, fluorohydrocarbons have other specialised industrial uses.

Alkyl halides may be regarded as derived from hydrocarbons by replacing one of the hydrogen atoms by a halogen atom. They may be sub - divided into classes according to the number of the alkyl groups attached to the carbon atom which is bonded to the halogen.

RCH_2X Primary alkyl halide.



Secondary alkyl halide



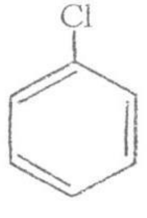
$$R-\underset{R''}{\overset{R'}{C}}-X$$

Tertiary alkyl halide

(X = chlorine, bromine or iodine)

Aryl halides

Aryl halides are halogen compounds in which the halogen atom is bonded to the carbon atom of the benzene ring. For example, chlorobenzene.



Dihalogen compounds

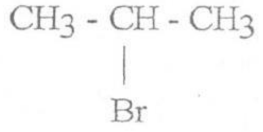
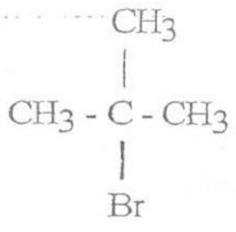
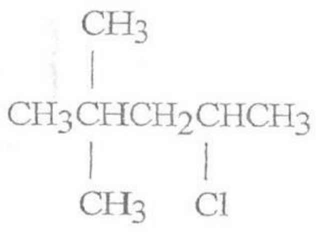
(a) Geminal (*gem-*) dihalides are compounds in which the two halogen atoms are bonded to the same carbon atom, RCX_2R', for example, $CH_3CH_2CCl_2CH_3$.

(b) Vicinal (*vic* -) dihalides are compounds in which the two halogen atoms are bonded to adjacent carbon atoms, $RCHX.CHXR'$, for example, $CH_3CHBr.CHBrCH_3$.

Nomenclature of alkyl halides

Alkyl halides are named as derivatives of the corresponding hydrocarbon. A number is inserted to indicate the position of the halogen in the carbon chain. In the nomenclature of branched chain halogen compounds, the alkyl substituents take precedence over the alkyl groups.

Examples

CH_3Cl	Chloromethane
CH_3CH_2Br	Bromoethane
$CH_3CH_2CH_2I$	1-Iodopropane
 $CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$	2-Bromopropane
 $CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$	2-Bromo-2-methylpropane
CH_3CHCH_2I	1-Iodo-2-methylpropane
 $CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}CH_2\underset{\underset{\displaystyle Cl}{|}}{CH}CH_3$	2-Chloro-4-methylpentane

Preparation of halogen compounds

Alkyl halides

(i) *From alkanes*

Alkanes undergo substitution reaction with halogens in the presence of sunlight. However, this is not a suitable method for the preparation of alkyl halides in the laboratory since a complex mixture of products are formed. (See chlorination of methane , page 16).

(ii) *From alkenes*

Hydrogen halides add across the alkene double bond to form alkyl halides (see under alkenes).

(iii) *From alcohols*

These reactions are discussed under alcohols.

Aryl halides

Aryl halides are prepared from benzene or its derivatives by reacting the aromatic hydrocarbon and the corresponding halogen in the presence of a halogen carrier as a catalyst (as discussed under aromatic hydrocarbons).

Physical properties of halogen compounds

Solubility

Organic halides are insoluble in water but are soluble in organic solvents and are miscible with each other. They are used as solvents.

Density

Alkyl chlorides are less dense than water but alkyl bromides and alkyl iodides are denser than water.

Boiling point

Chloromethane, chloroethane and bromomethane are gases at room temperature. The rest are liquids. Since there are no complications due to hydrogen bonding, the boiling points of alkyl halides increase with increase in the molecular mass of the alkyl halide. For a given alkyl group, the boiling point increase in the order $RI > RBr > RCl$.

Densities and boiling points of some halogen compounds

Hydrocarbon part	*Chloride*		*Bromide*		*Iodide*	
	B.p. °C	Density	B.p. °C	Density	B.p. °C	Density
CH_3-	-23.8	0.92	3.6	1.75	42.5	2.84
CH_3CH_2-	13.1	0.91	38.4	1.46	72	1.95
$CH_3CH_2CH_2$-	46.6	0.89	70.8	1.35	102	1.74
$(CH_3)_2CH$-	34	0.86	59.4	1.31	89.4	1.7
$CH_3CH_2CH_2CH_2$-	78.4	0.89	101	1.27	130	1.61
$CH_3CH_2(CH_3)CH$-	68	0.87	91.2	1.26	120	1.6
$(CH_3)_2CHCH_2$-	69	0.87	91	1.26	119	1.6
$(CH_3)_3C$-	51	0.84	73.3	1.22	100(dec.)	1.57

Reactions of alkyl halides

Nucleophilic substitution reaction

Nucleophilic substitution reaction is a reaction in which one atom or group of atoms that can donate an electron pair i.e. ***nucleophile*** replaces another atom or group of atoms attached to a saturated carbon atom. The displaced substituent is called a ***leaving group*** and normally departs with the pair of electrons which had composed the bond. The nucleophile (which can be an anion or a neutral molecule must contain a non-bonded pair of electrons) uses the unshared electrons to form the new bond to carbon.

In alkyl halides, the electrons forming the carbon - halogen bond is not shared equally. It is displaced more towards the halogen atom. This is because a halogen atom is more electronegative than carbon atom. The carbon -halogen bond is thus polar, with the carbon being slightly positively charged and the halogen slightly negatively charged. The permanent separation of charge in the carbon - halogen bond is an example of ***inductive effect*** and results in the molecule having a dipole moment.

$$^{\delta+}C \longrightarrow X^{\delta-}$$

inductive effect

The polarity of the carbon - halogen bond makes the halogen atom a good leaving group and the slight positive charge on the carbon makes it prone to nucleophilic attack. Thus if a nucleophile approaches the positive carbon, the slightly negative halogen is repelled and finally displaced by the incoming group. The most important reactions of alkyl halides are therefore nucleophilic substitution reactions. Since the reactions lead to the introduction of various functional groups into the molecule, they are of great importance in organic synthesis as shown in the table below.

Displacement reactions of alkyl halide , RX

Nucleophile		*Product*	
Formula	*Name*	*Formula*	*Name*
^-OH	hydroxide ion	ROH	alcohol
H_2O	water	ROH	alcohol
$^-OR'$	alkoxide ion	ROR'	ether
NH_3	ammonia	RNH_2	primary amine
$R'NH_2$	primary amine	RNHR'	secondary amine
R'_2NH	secondary amine	RNR'_2	tertiary amine
$^-C{\equiv}N$	cyanide ion	$R-C{\equiv}N$	nitrile
$HC{\equiv}C^-$	acetylide ion	$RC{\equiv}CH$	higher alkyne
CH_3COO^-	ethanoate ion	CH_3CO_2R	ester

Mechanism of nucleophilic reaction

There are two possible ways in which a nucleophilic reaction can proceed:

(a) The formation of the new bond with the nucleophile and the breaking of the old bond with the leaving group could take place simultaneously. This is known as a one step concerted process. Primary alkyl halides tend to react by this mechanism.

(b) The old bond with the leaving group is broken first and then the new bond with the nucleophile is formed. This is known as a two step process. Tertiary alkyl halides are known to react by this mechanism.

One step, concerted mechanism

Hydrolysis of bromomethane

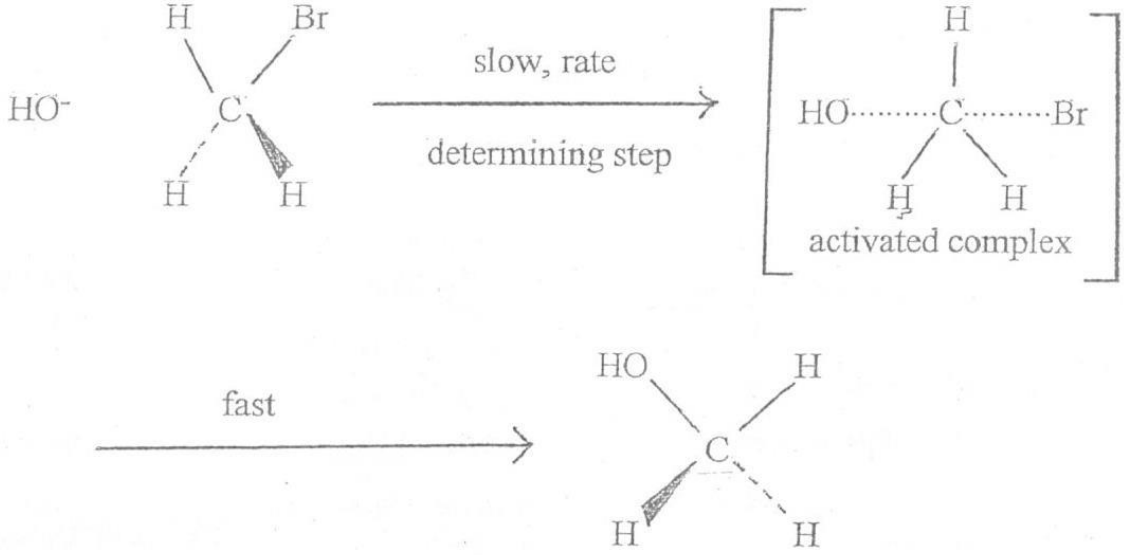
When bromomethane is reacted with aqueous sodium hydroxide it is converted to methanol.

$$CH_3Br + NaOH \xrightarrow{heat} CH_3OH + NaBr$$

It was found from kinetics studies that the rate of the reaction depends on the concentration of the hydroxide ion and the alkyl halide.

i.e. Rate $=$ $k[^{-}OH][CH_3Br]$ where k is the rate constant.

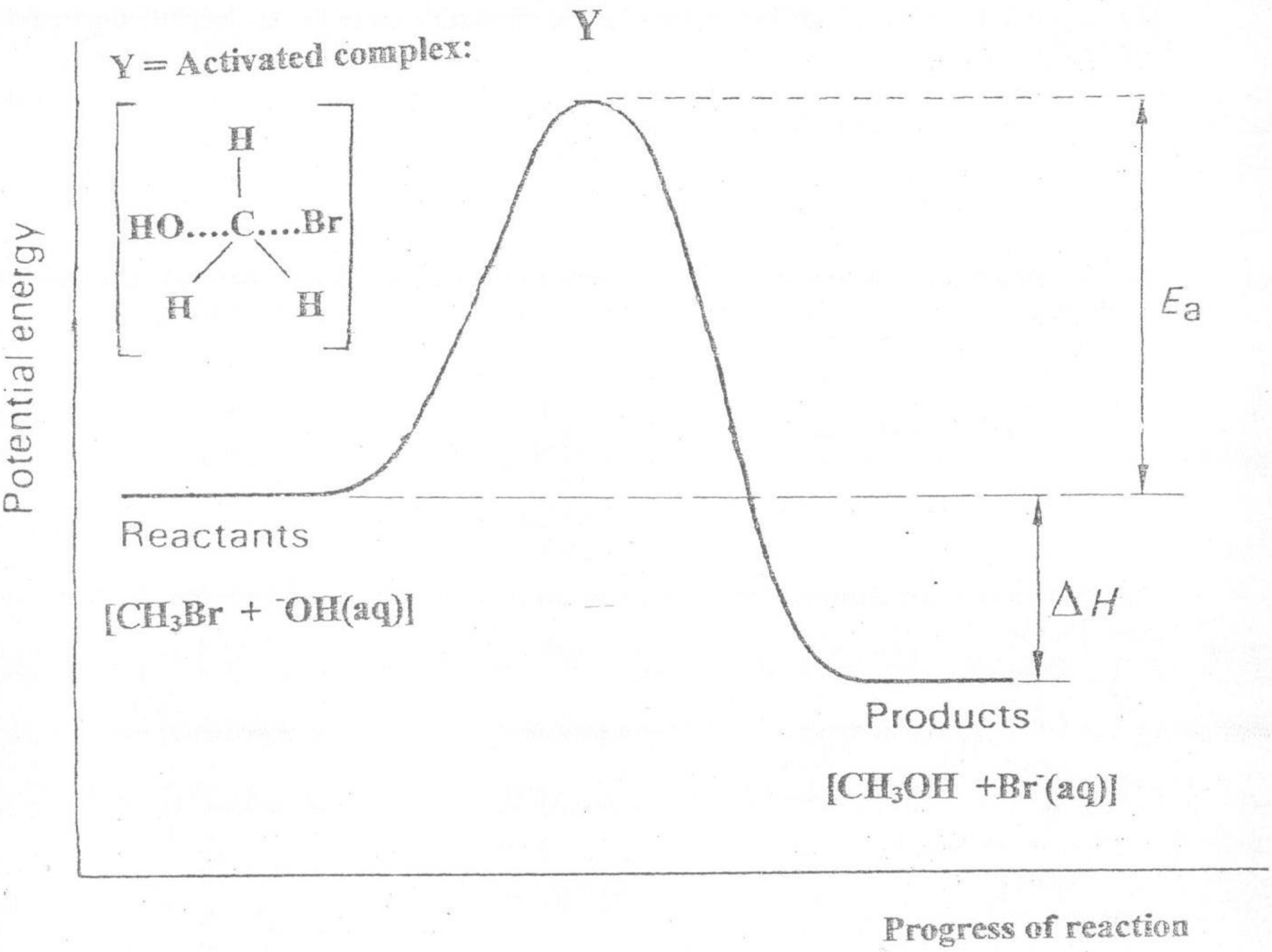
This means that it is a bimolecular reaction in which the slow and therefore rate determining step involves both the hydroxide ion and bromomethane.



The slow and therefore the rate determining step is the nucleophilic attack by the hydroxide ion on the carbon atom from the side opposite the bromine i.e. backside attack by the nucleophilic reagent to form an ***activated complex.*** The activated complex may be regarded as some arrangement of atoms in which there is partial formation of a bond between oxygen of the hydroxide ion and carbon, and at the same time there is partial cleavage of the bond between the bromine atom and carbon. The three hydrogen atoms are in the same plane with the carbon atom in the activated complex and are in a plane perpendicular to the plane of this paper. The cleavage of the bromine - carbon bond to give methanol and the bromide ion is fast. The reaction is known as ***Substitution Nucleophilic Bimolecular*** abbreviated S_N2. It is called bimolecular because the formation of the activated complex involves two species, the alkyl halide and the nucleophile.

The arrangement of the three groups attached to the carbon atom in the product differs from that of the starting material in that it has been turned inside out. The carbon atom is said to have undergone inversion of its configuration i.e. the reaction proceeds with inversion of configuration at the centre of attack.

Energy diagram for one step (S_N2) reaction



E_a = Energy of activation

In the energy diagram for S_N2 reaction there is only one maximum representing one transition state.

Two step mechanism

Hydrolysis of 2-bromo-2-methylpropane (tert-butyl bromide)

2-Bromo-2-methylpropane reacts with aqueous sodium hydroxide to give 2-methylpropan-2-ol.

$$(CH_3)_3CBr \quad + \quad {}^-OH(aq) \quad \rightarrow \quad (CH_3)_3COH \quad + \quad Br^-(aq)$$

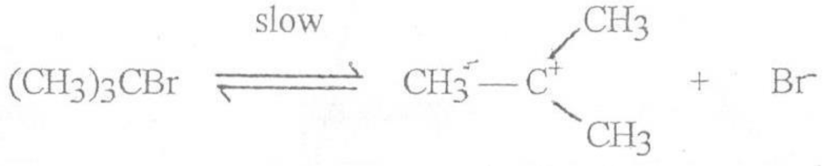
Mechanism

It was found from kinetics studies that the rate of the reaction depends on the concentration of the alkyl halide only and was independent of the concentration of the nucleophile (hydroxide ion in this case).

$$\text{Rate} = k[(CH_3)_3CBr]$$

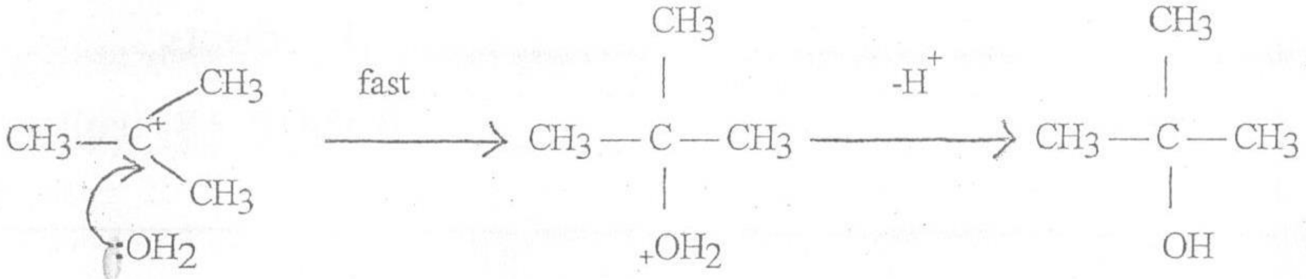
This means that it is a unimolecular reaction.

The first step of the reaction is the slow reversible ionisation of the alkyl halide to produce the highly reactive carbonium ion and a bromide ion. This is the rate determining step.



A carbonium ion

The carbonium ion formed rapidly reacts with water or hydroxide ion to form 2-methylpropan-2-ol.

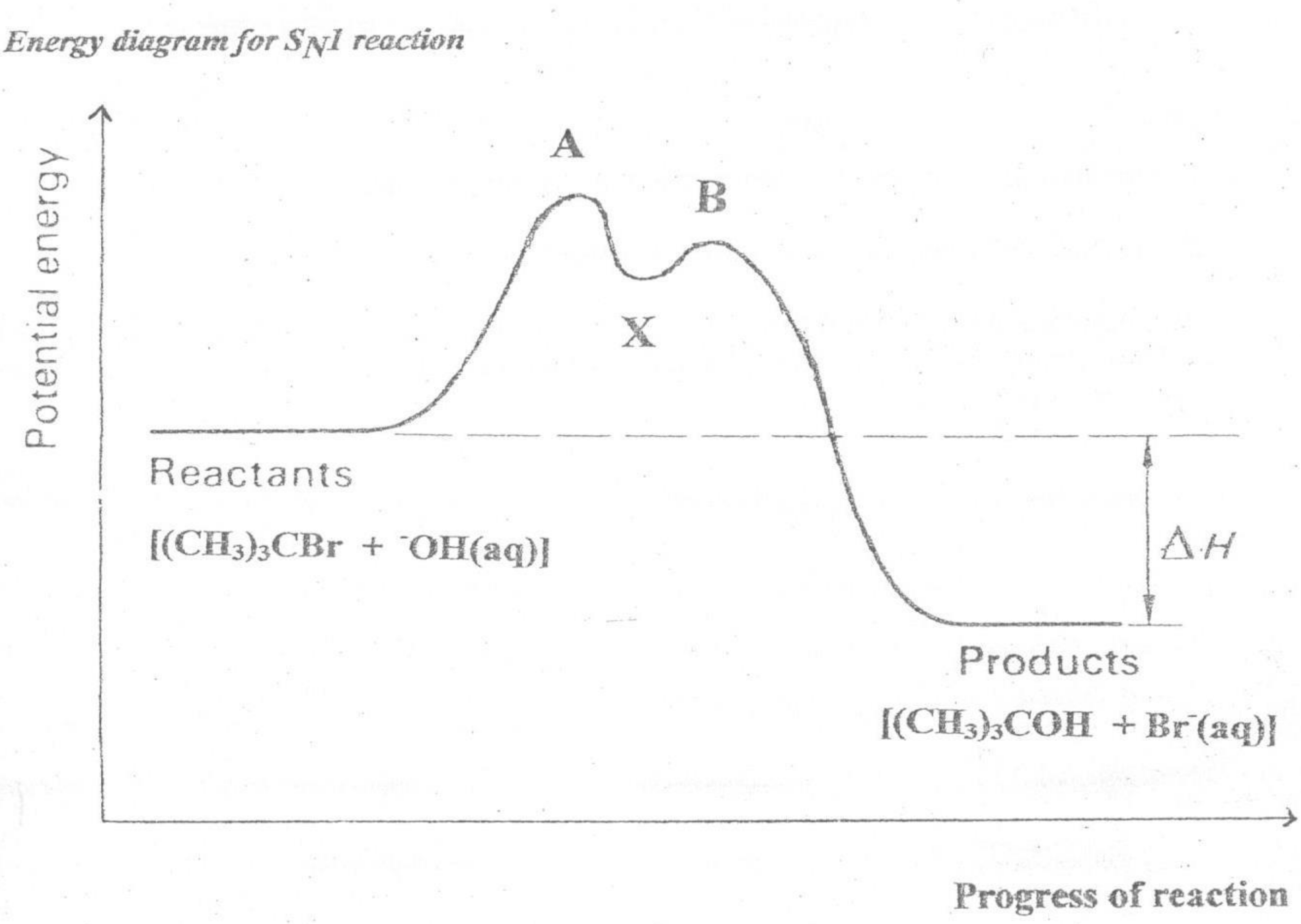


This type of mechanism is known as ***Substitution Nucleophilic Unimolecular ,S_N1 reaction.*** It is unimolecular because the slow and therefore the rate determining step is the ionisation of the alkyl halides i.e. involves one species only.

Energy diagram for the S_N1 reaction

In the energy diagram for S_N1 reaction, the formation of the carbonium ion (intermediate) corresponds to a minimum and there are two maxima corresponding to the two transition states related to the two reaction steps. The higher transition state A determines the overall two-step reaction rate.

Energy diagram for S_N1 reaction



A = Transition state A: $[(CH_3)_3C \ldots. Br]$

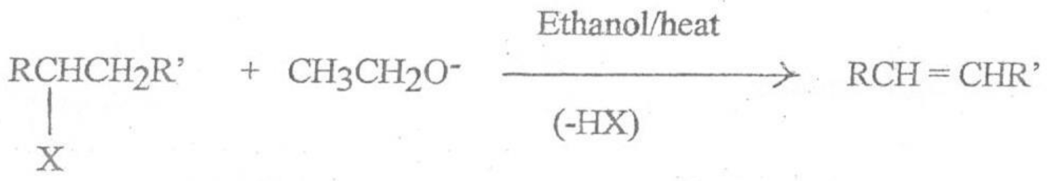
B = Transition state B: $[(CH_3)_3C \ldots. OH]$

X = Intermediate: $(CH_3)_3C^+)$

Tertiary alkyl halides tend to react by S_N1 mechanism while primary alkyl halides tend to follow S_N2 mechanism. Secondary alkyl halides react partly by S_N1 and partly by S_N2 mechanisms.

Elimination reaction

When alkyl halides are heated under reflux with ethanolic solution of potassium hydroxide or a solution of sodium ethoxide in ethanol, an alkene is formed. This is known as an ***elimination reaction*** since the final product is formed by a loss (or elimination) of a molecule of hydrogen halide from the starting organic molecule. The reaction involves the removal of a halogen as halide ion together with a hydrogen atom as a proton. The hydrogen atom removed is the one bonded to the carbon atom adjacent to the one bonded to the halogen

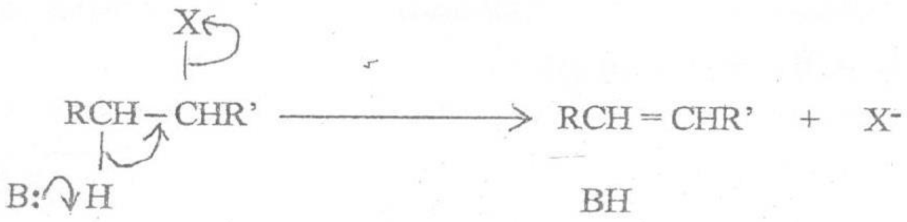


$$RCH(X)CH_2R' + CH_3CH_2O^- \xrightarrow[(-HX)]{Ethanol/heat} RCH=CHR'$$

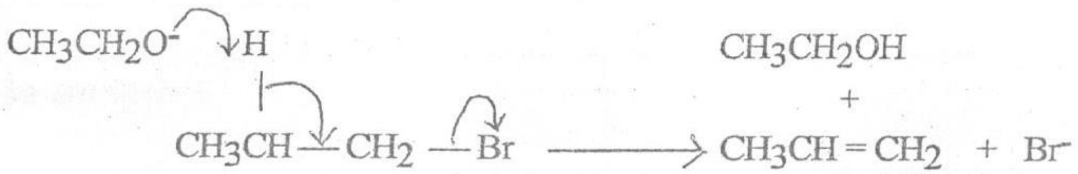
Elimination reactions can proceed by two types of mechanisms.

Bimolecular elimination reaction (E2 reaction)

Bimolecular elimination reaction is a one step reaction. The removal of the proton by the base and the cleavage of the carbon - halogen bond occur simultaneously. The reaction can be represented as follows:



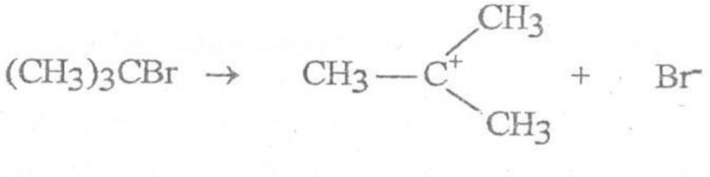
Example



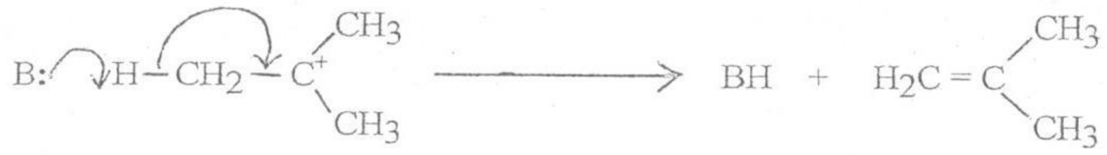
The reaction is called Elimination Bimolecular (E2) because two species, the base and the alkyl halide are involved in the formation of the transition state. Primary alkyl halides generally react by this mechanism.

Unimolecular Elimination (E1) reactions

This is a two step reaction. The first step involves the slow ionisation of the alkyl halide to form a carbonium ion.



In the second step, a hydrogen atom bonded to a carbon atom adjacent to the positively charged carbon atom is removed by the base or solvent.



Tertiary alkyl halides tend to react by this mechanism.

Reduction of alkyl halides

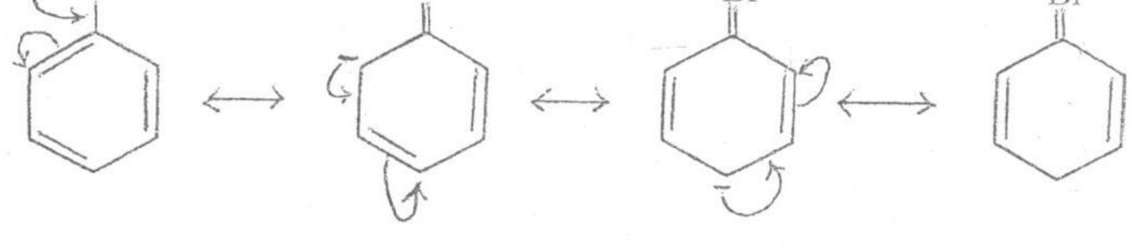
(See under preparation of alkanes).

REACTIONS OF AROMATIC HALIDES

Reaction with nucleophiles

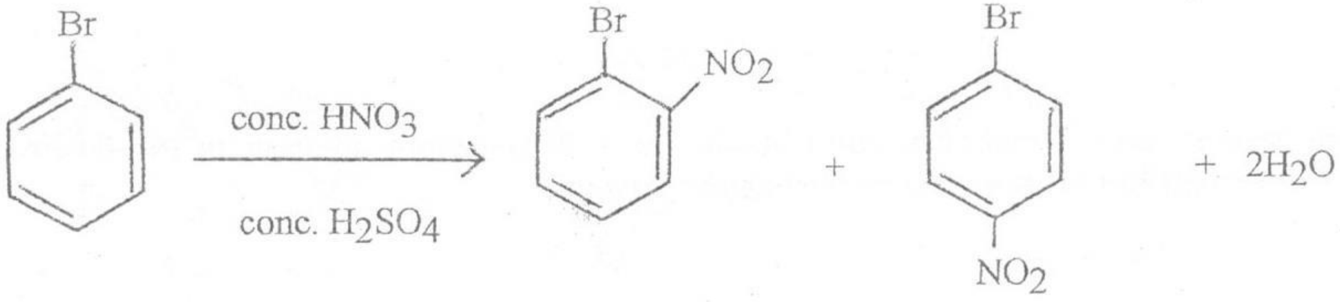
Aromatic halides are unreactive towards nucleophiles. Hence they do not undergo nucleophilic substitution reactions except under drastic conditions. For example in the manufacture of phenols, chlorobenzene is heated with sodium hydroxide at 200° C under pressure (200 atmospheres).

The reason for the difference in the reactivity of aromatic halides towards nucleophiles is that the carbon - halogen bond in aromatic halides is stronger than the one in alkyl halides. This is because the non - bonded electrons on the halogen atom interacts with the delocalised p - electron system of the benzene ring as shown in the structures below in which three structures show carbon - bromine bond
and positive charge on the bromine atom.



Electrophilic substitution reactions

Aryl halides undergo electrophilic substitution in the benzene ring when reacted with electrophilic reagents. The halogen group directs the incoming substitution to the *ortho* and *para* positions.


Br
conc. HNO_3
conc. H_2SO_4
Br
NO_2
+
Br
NO_2
+ $2H_2O$

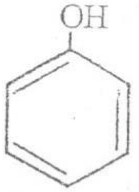
CHAPTER 8

HYDROXY COMPOUNDS (ALCOHOLS AND PHENOLS)

Introduction

Alcohols are compounds that contain the hydroxyl (OH) group bonded to a saturated carbon atom. They may be regarded as derivatives of alkanes in which one of the hydrogen atoms is replaced by the OH group or as derivatives of water in which one of the hydrogen atoms is replaced by an alkyl group.
ROH.

Phenols are compounds in which the OH group is bonded to a carbon atom of the benzene ring.



Phenol (hydroxybenzene)

Classification of alcohols

Classification according to the number of OH groups

Alcohols may be classified according to the number of OH groups in the molecule:

i) Monools (monohydric alcohols) contain one OH group e.g. CH_3CH_2OH;

ii) Diols (dihydric alcohols) contains two OH groups e.g. $HOCH_2CH_2OH$;

iii) Triols (trihydric alcohols) contain three OH groups e.g. $HOCH_2CH(OH)CH_2OH$;

iv) Polyols (polyhydric alcohols) contain many OH groups e.g. sugars.

Classification of monools

Monools are further sub-divided according to the number of the alkyl groups attached to the carbon atom bonded to the OH group. The carbon atom bonded to the OH group is called a -carbon and the hydrogen(s) bonded to it is(are) known as a - hydrogen(s).

(a) Primary alcohols contain two α - hydrogens, e.g. CH_3CH_2OH.

(b) Secondary alcohols contain one α - hydrogen e.g. $(CH_3)_2CHOH$.

(c) Tertiary alcohols do not contain any α - hydrogen e.g. $(CH_3)_3COH$.

Nomenclature of alcohols

In the nomenclature of alcohols, the longest chain of carbon atoms containing the hydroxyl group is chosen and numbered to give the carbon atom attached to the OH group the lowest possible number. The suffix ***-ol*** is used instead of the last ***-e*** in the name of the corresponding alkane.

Nomenclature of alcohols

Structure of alcohol	*IUPAC Name*	*Common name*
CH_3OH	Methanol	Methyl alcohol
CH_3CH_2OH	Ethanol	Ethyl alcohol
$CH_3CH_2CH_2OH$	Propan-1-ol	n-Propyl alcohol
$CH_3CH(OH)CH_3$	Propan-2-ol	*iso*-Propyl alcohol
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	n-Butyl alcohol
$CH_3CH(OH)CH_2CH_3$	Butan-2-ol	*sec*-Butyl alcohol
$CH_3CH(CH_3)CH_2OH$	2-Methylpropan-1-ol	*iso*-Butyl alcohol
$CH_3C(CH_3)(OH)CH_3$	2-Methylpropan-2-ol	*tert*-Butyl alcohol

Physical properties of alcohols

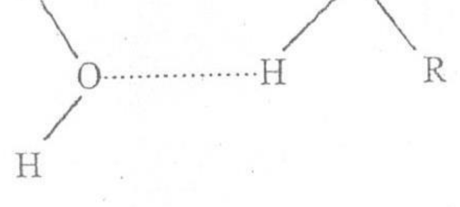
The variation in the physical properties of some alcohols is shown in the table below.

Structure	*Name*	*m.p (°C)*	*b.p. (°C)*	*Density (25 °C)*	*sol. in H_2O (g/100 H_2O)*
CH_3OH	Methanol	-97	65	0.792	infinity
CH_3CH_2OH	Ethanol	-114	78	0.789	infinity
$CH_3CH_2CH_2OH$	Propan-1-ol	-126	97	0.804	infinity
$CH_3CH(OH)CH_3$	Propan-2-ol	-88	82	0.786	infinity
$CH_3CH_2CH_2CH_2OH$	Butan-1-ol	-90	118	0.81	7.9
$CH_3CH(CH_3)CH_2OH$	2-Methylpropan-1-ol	-108	108	0.802	10
$CH_3CH_2CH(OH)CH_3$	Butan-2-ol	-114	99.5	0.808	12.5
$(CH_3)_3COH$	2-Methylpropan-2-ol	25	82.5	0.789	infinity
$CH_3(CH_2)_3CH_2OH$	Pentan-1-ol	-78.5	138	0.817	2.4
$CH_3(CH_2)_4CH_2OH$	Hexan-1-ol	-52	156.5	0.919	0.6
$CH_3(CH_2)_5CH_2OH$	Heptan-1-ol	-34	176	0.822	0.2

Boiling points of alcohols

Alcohols boil at much higher temperature than expected from their molecular mass. Thus, although methanol and ethane have approximately the same molecular mass, 32 and 30 respectively, their boiling points are respectively 65 °C and -87 °C. Ethanol (molecular mass 46) boils at 78 °C while propane (molecular mass 44) boils at -44.5 °C.

The reason is that molecules of alcohols, like those of water are associated through hydrogen bonding. Hence extra energy is required to break the hydrogen bond before the molecules can be separated.

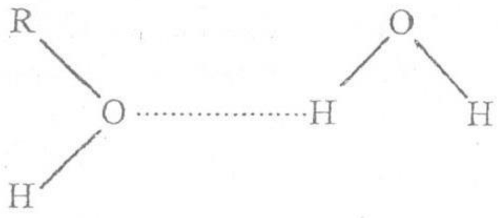


Hydrogen bonding in alcohol

Within the series, the boiling points of alcohol increases with increase in molecular mass.

Solubility of alcohols

Lower members of the alcohol series are soluble in water. Thus, methanol, ethanol, propanols and 2-methylpropan-2-ol are miscible with water in all proportions. However, solubility in water gradually decreases as the hydrocarbon chain of the molecule increases. The solubility of alcohols in water is due to the fact that they are capable of forming hydrogen bonding with water molecules.



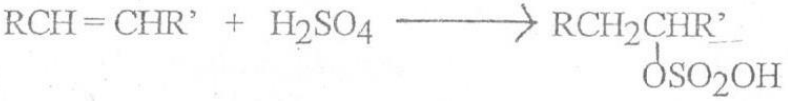
Hydrogen bonding between alcohol and water molecules

Long chain alcohols are 'alkanelike' and are therefore less like water and are therefore not soluble in water.

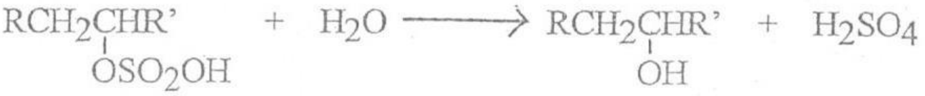
Methods for the preparation of alcohols

From alkenes

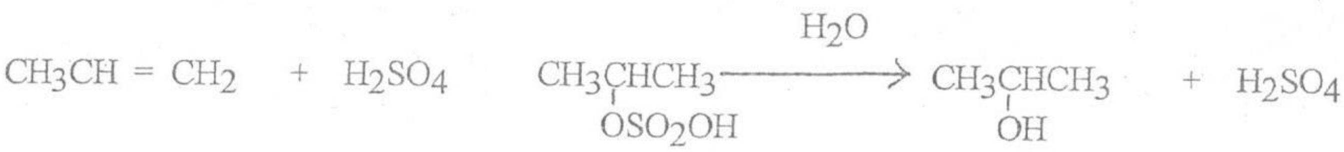
Alcohols are formed when alkenes are reacted with concentrated sulphuric acid followed by hydrolysis of the product with water.



$$RCH=CHR' + H_2SO_4 \longrightarrow RCH_2\underset{OSO_2OH}{\underset{|}{C}}HR'$$



$$RCH_2\underset{OSO_2OH}{\underset{|}{C}}HR' + H_2O \longrightarrow RCH_2\underset{OH}{\underset{|}{C}}HR' + H_2SO_4$$



$$CH_3CH = CH_2 + H_2SO_4 \quad CH_3\underset{OSO_2OH}{\underset{|}{C}}HCH_3 \xrightarrow{H_2O} CH_3\underset{OH}{\underset{|}{C}}HCH_3 + H_2SO_4$$

From alkyl halides

Alkyl halides are hydrolysed by hot aqueous sodium hydroxide solution to give alcohols.

$$RBr + {}^{-}OH(aq) \xrightarrow{\text{heat}} ROH + Br^{-}(aq)$$

From esters

Esters are hydrolysed by dilute aqueous mineral acids or aqueous sodium hydroxide solution to alcohols and carboxylic acids. However, this is not the normal method for preparing alcohols since esters are usually prepared from alcohols.

$$RCO_2R' + {}^{-}OH(aq) \xrightarrow{\text{heat}} RCO_2{}^{-}(aq) + R'OH$$

$$RCO_2R' + H^{+}(aq) \xrightarrow{\text{heat}} RCO_2H + R'OH$$

From carbonyl compounds

Aldehydes on reduction give primary alcohols and ketones are reduced to secondary alcohols.

$$\underset{\text{Aldehyde}}{RCHO} + [H] \rightarrow RCH_2OH$$

$$\underset{\text{Ketone}}{RCOR'} + [H] \rightarrow RCH(OH)R'$$

The reducing agents commonly used are Zn/H^+ (CH_3CO_2H or HCl); Na - Hg/water; Na/ethanol; finely divided Ni or Pt with hydrogen gas; lithium aluminium hydride ($LiAlH_4$). Lithium aluminium hydride does not reduce a double bond.

Reactions of alcohols

Acidity and basicity of alcohols

Although alcohols are neutral to acid/base indicators, the hydrogen of the OH group can be replaced by electropositive metals (groups I and II metals in the Periodic Table). The products are hydrogen gas and the metal alkoxide.

$$2CH_3CH_2OH + 2Na \rightarrow \underset{\text{Sodium ethoxide}}{2CH_3CH_2O^{-}Na^{+}} + H_2$$

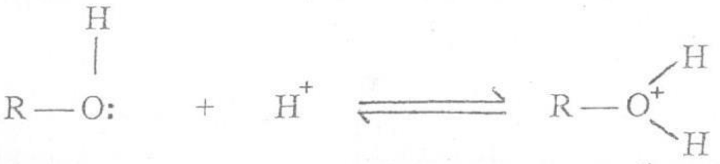
$2CH_3OH + 2Mg \rightarrow 2CH_3O^- Mg^{2+} + H_2$

Magnesium methoxide

In these reactions alcohols are behaving as very weak acids.

Alcohols as very weak bases

The oxygen atoms in an alcohol has a lone pair of electrons. In the presence of an acid, alcohols react with the acid to form a protonated alcohols. Protonated alcohols are stable in solutions only. They cannot be isolated.



Protonated alcohol

Esterification of alcohols

Esters are formed when alcohols are reacted with acid chlorides, acid anhydrides or carboxylic acids in the presence of a mineral acid.

Reaction with acid chloride (agylation)

$RCOCl + R'OH \rightarrow RCO_2R' + HCl$

$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + HCl$

Ethanoyl chloride, Ethanol, Ethyl ethanoate

Reaction with acid anhydride

$(RCO)_2O + R'OH \rightarrow RCO_2R' + RCO_2H$

$(CH_3CO)_2O + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + CH_3CO_2H$

Ethanoic anhydride, Ethanol, Ethyl ethanoate, Ethanoic acid

Reaction with carboxylic acids

Alcohols react with carboxylic acids in the presence of concentrated sulphuric acid to form esters. The reaction is reversible.

$$RCO_2H + R'OH \rightleftharpoons RCO_2R' + H_2O$$

$$CH_3CO_2H + CH_3OH \rightleftharpoons \underset{\text{Methyl ethanoate}}{CH_3CO_2CH_3} + H_2O$$

Reactions involving the cleavage of the C - O bond

Reaction with hydrogen halides

Alcohols react with hydrogen halides to form alkyl halides.

$$ROH + HX \longrightarrow RX + H_2O$$

For alcohols, the order of reactivity is tertiary > secondary > primary while the order of reactivity of hydrogen halides is HI > HBr > HCl.

In the case of hydrogen chloride, the reaction is normally carried out using a solution of anhydrous zinc chloride in concentrated hydrochloric acid. The solution is known as Luca's reagent and is used in a test to distinguish between primary, secondary and tertiary alcohols. If a sample of tertiary alcohol is shaken with Luca's reagent at room temperature, reaction takes place immediately and a cloudy solution , due to the formation of an alkyl halide is observed. In some cases two layers of liquids are formed: the aqueous layer and the organic (alkyl halide) layer. With secondary alcohols the reaction takes place within five to ten minutes i.e. cloudiness or two layers of liquids are observed within five to ten minutes. For primary alcohols, the reaction does not take place at room temperature.

Reactions with phosphorus halides and thionyl chloride

Alcohols react with phosphorus tribromide and phosphorus triiodide to form alkyl bromide and alkyl iodides respectively.

$$3ROH + PBr_3 \rightarrow RBr + H_3PO_3$$

$$3ROH + PI_3 \rightarrow RI + H_3PO_3$$

The reaction is normally carried out using phosphorus halide prepared in *situ* using red phosphorus and the halogen.

Phosphorus pentachloride and thionyl chloride convert alcohols to alcohols to alkyl chlorides. Reaction with thionyl chloride is best with primary alcohols.

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

$$\underset{\text{Thionyl chloride}}{RCH_2OH + SOCl_2} \rightarrow RCl + SO_2 + HCl$$

Reaction with sulphuric acid

The product of the reaction between an alcohol and sulphuric acid depends on the class of alcohol and the conditions under which the reaction is carried out.

(a) At lower temperatures, the product is an alkyl hydrogen sulphate.

$$ROH + \text{conc. } H_2SO_4 \rightarrow ROSO_2OH + H_2O$$

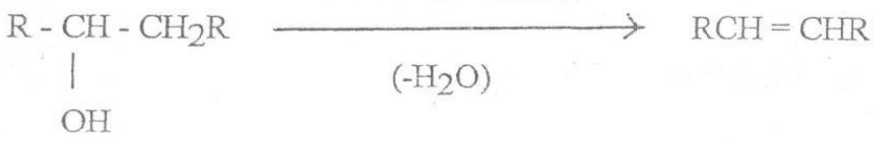
$$CH_3CH_2OH + \text{conc. } H_2SO_4 \rightarrow CH_3CH_2OSO_2OH + H_2O$$

(b) When the reaction is carried out at about 140^o C using excess of alcohol, the product is an ether.

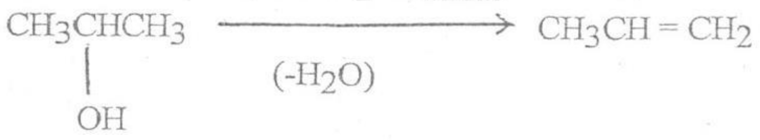
$$2ROH + \text{conc. } H_2SO_4 \xrightarrow{140^o} ROR + H_2O$$

$$2CH_3CH_2OH + \text{conc. } H_2SO_4 \xrightarrow{140^o} \underset{\text{Ethoxyethane}}{CH_3CH_2OCH_2CH_3} + H_2O$$

(c) When a mixture of alcohol and excess concentrated sulphuric acid or concentrated orthophosphoric acid is heated at about 180^o C, a molecule of water is eliminated from the alcohol and an alkene is formed.



$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2R \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_{4/heat}} RCH=CHR$$

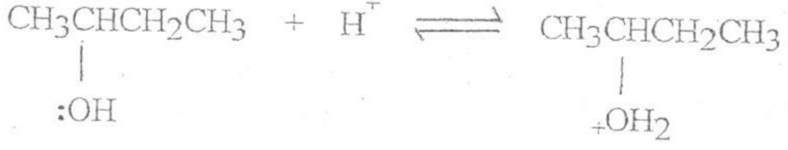


$$CH_3\underset{\displaystyle OH}{\underset{|}{CH}}CH_3 \xrightarrow[(-H_2O)]{\text{Conc. } H_2SO_{4/heat}} CH_3CH=CH_2$$

This is an example of elimination reaction. The reaction is also known as dehydration of alcohols.

Mechanism

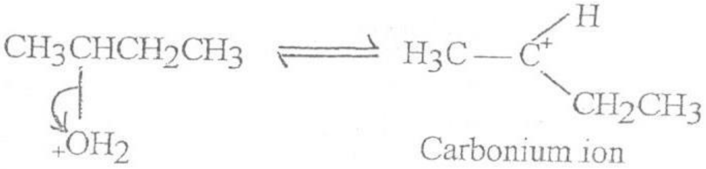
The first step of the reaction is the protonation of the alcohol by the acid.



$$\underset{:OH}{CH_3CHCH_2CH_3} + H^+ \rightleftharpoons \underset{+OH_2}{CH_3CHCH_2CH_3}$$

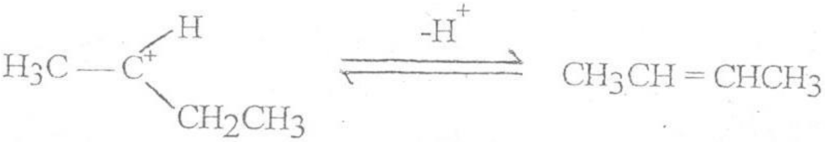
protonated alcohol

The next step which is slow and therefore determines the overall rate of the reaction is the loss of water from the protonated alcohol to give a carbonium ion.



Carbonium ion

The last step is the rapid loss of a proton from the carbon atom which is adjacent to the one carrying the positive charge.

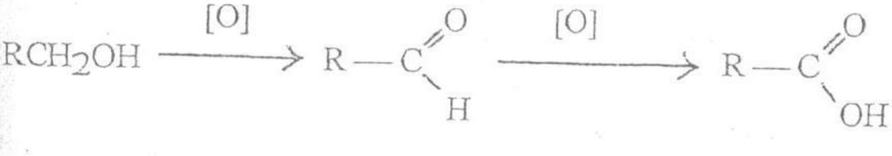


Alcohols can also be dehydrated using concentrated orthophosphoric acid or by passing of the alcohol over heated aluminium oxide.

Oxidation of alcohols

The product of the oxidation of alcohols depends on the class of the alcohol.

Primary alcohols are oxidised to aldehydes which in turn may be oxidised to carboxylic acids.



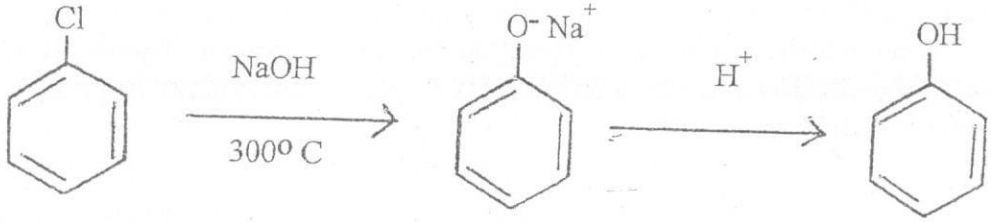
The oxidation is normally brought about in solution by basic or acidified potassium permanganate solution or by acidified sodium dichromate or acidified chromium trioxide solution.

Industrial preparation of phenol

(a) Benzene sulphonic acid process (as described above)

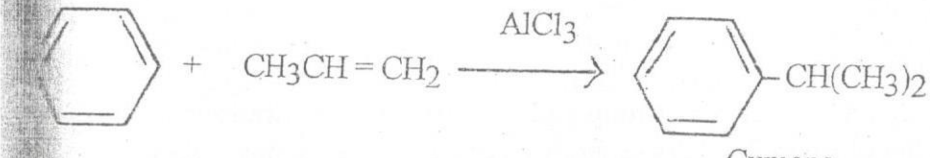
(b) Chlorobenzene process

Chlorobenzene, obtained from benzene as already described, is heated with sodium hydroxide at 300⁰ under pressure and the sodium phenate formed is reacted with a mineral cid to form phenol.



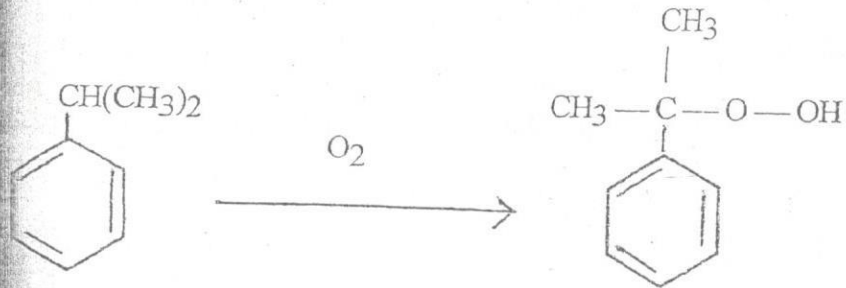
) The cumene process

the cumene process, benzene is first alkylated with propene using aluminium chloride as a alyst or in gaseous phase with phosphoric acid to form cumene.



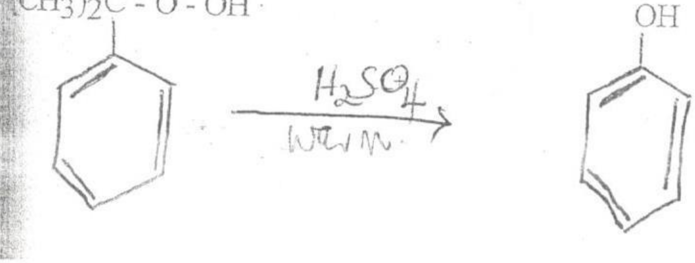
Cumene

is then passed through the cumene to form cumene hydroperoxide.

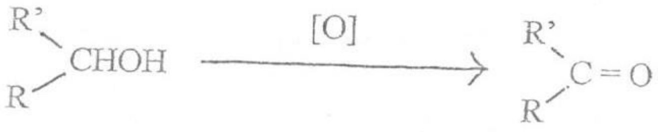


Cumene hydroperoxide

umene hydroperoxide is decomposed with warm, dilute sulphuric acid.



Secondary alcohols are oxidised to ketones. The reaction can be brought about by a number of oxidising agents but the most commonly used is acidified chromium trioxide.



Tertiary alcohols are not easily oxidised. Oxidation under drastic conditions leads to breaking of carbon - carbon bond.

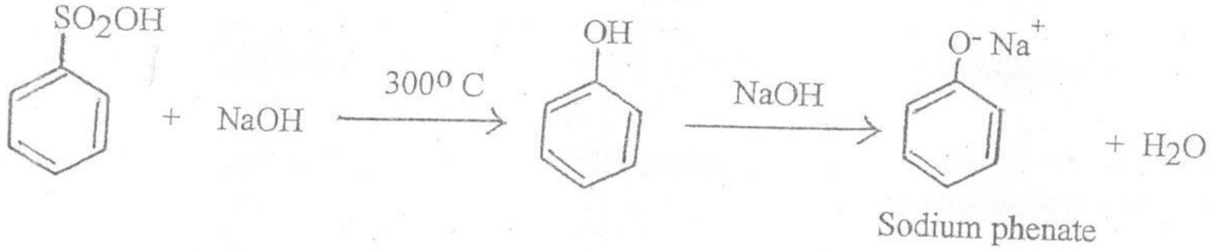
PHENOL

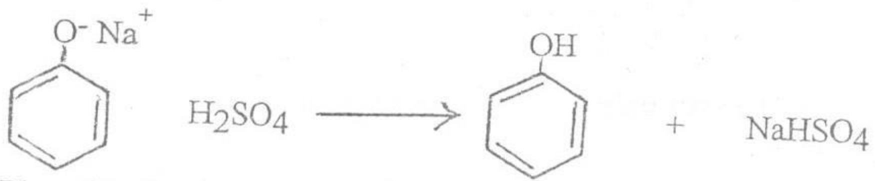
Physical properties of phenol

Phenol is a colourless crystalline solid, which melts at 42^0 C and boils at 182^0 C. When exposed to air or light, phenol becomes coloured. It is slightly soluble in water (more soluble than cyclohexanal) but very soluble in organic solvents. Phenol forms stronger bonding than alcohols.

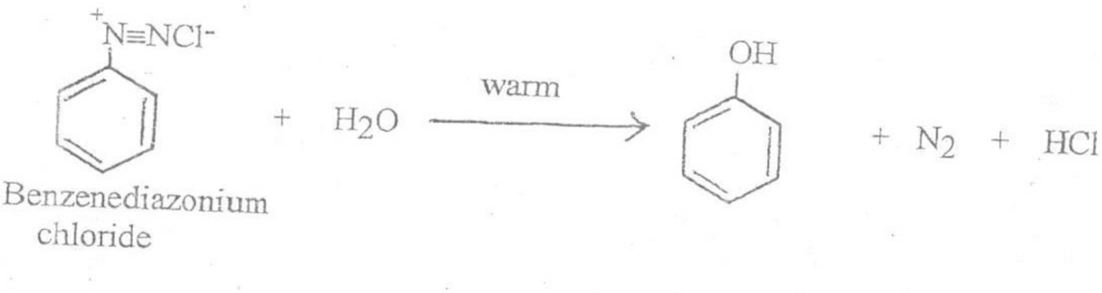
Preparation of phenol

(a) Phenol is prepared by fusing benzene sulphonic acid (obtained by sulphonation of benzene) with sodium hydroxide at 300^0 C.





(b) Phenol is formed when an aqueous solution of benzenediazonium salt is warmed.

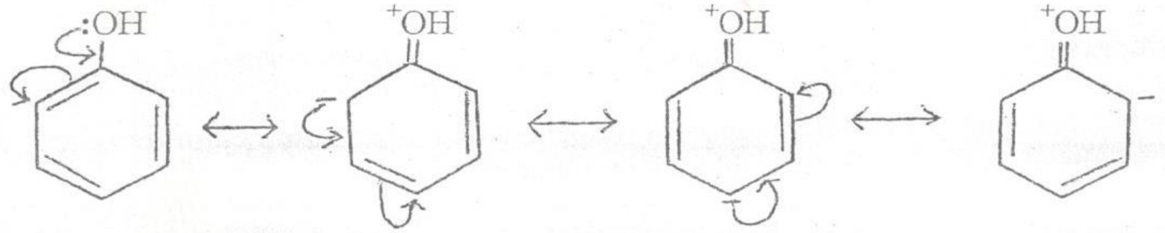


Reactions of phenol

Phenol as an acid

Phenol is a weak acid ($K_a = 1.3 \times 10^{-10}$). It is a stronger acid than alcohols but weaker than carboxylic acids and carbonic acid ($K_a = 4.3 \times 10^{-7}$). Phenol therefore does not liberate carbon dioxide from carbonates and hydrogen carbonates. An aqueous solution of phenol is acidic to litmus and react with sodium hydroxide to form sodium phenate which is soluble in water. Phenol is therefore soluble in sodium hydroxide solution.

The acidity of phenol shows that the O - H bond in phenol is weaker than the O - H bond in alcohols. This is explained by the fact that in phenol, the lone pairs of electrons on the oxygen atom become associated with the delocalised π - electrons of the benzene ring thus strengthening the C - O bond, which then acquires partial double bond character. The O - H bond is thus weakened as the electron density of this bond is displaced towards the benzene ring hence giving phenol an acidic nature.



Reaction of the OH group

(a) As explained above, the C - O bond in phenol is strong and the OH group is firmly held and is thus not easily replaced. Phenol, therefore, differ from alcohols in that it does react with halogen acids or phosphorus halides to form the corresponding halobenzene.

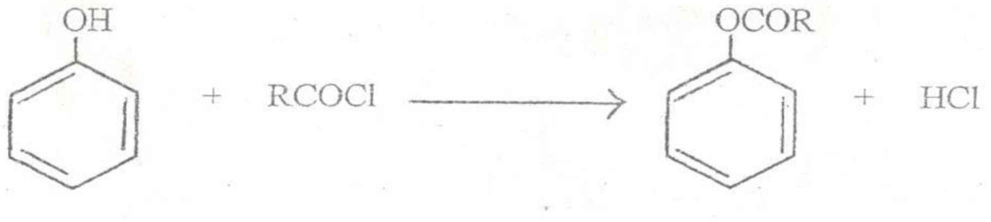
(b) Phenol differs from alcohols in that

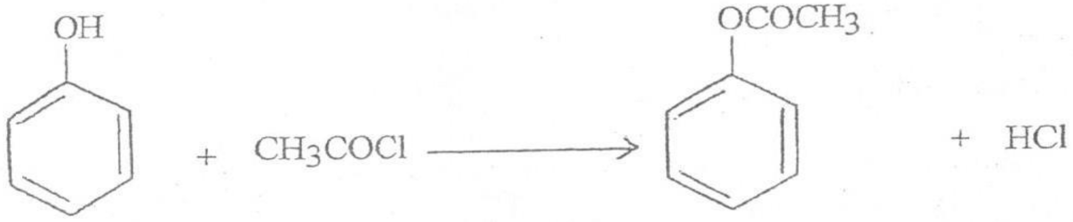
(i) it does not undergo elimination reaction;

(ii) it is easily oxidised but not in the same way as alcohols. The products are usually complex.

Reactions in which phenols resemble alcohols

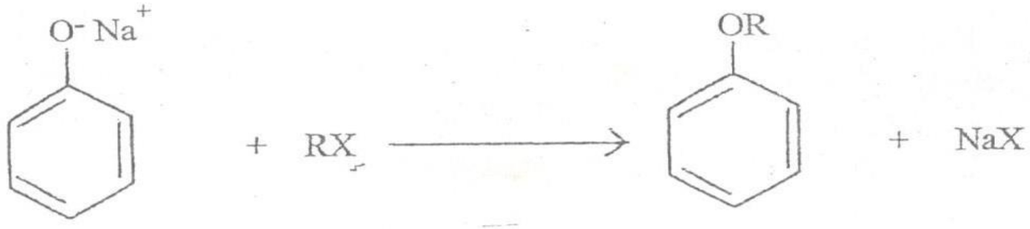
(a) Phenol reacts with acid chlorides and acid anhydrides to form esters.





Phenyl ethanoate

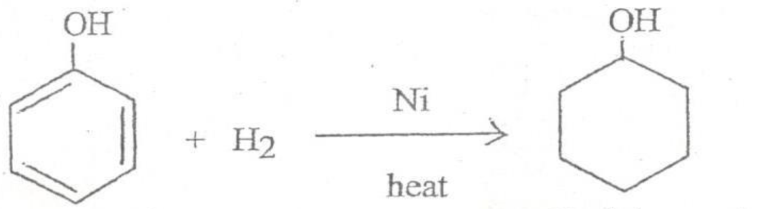
(b) Sodium phenate form ethers when heated with alkyl halides.



Reactions of the benzene ring

Reduction

Phenol is reduced by hydrogen in the presence of nickel to cyclohexanol.

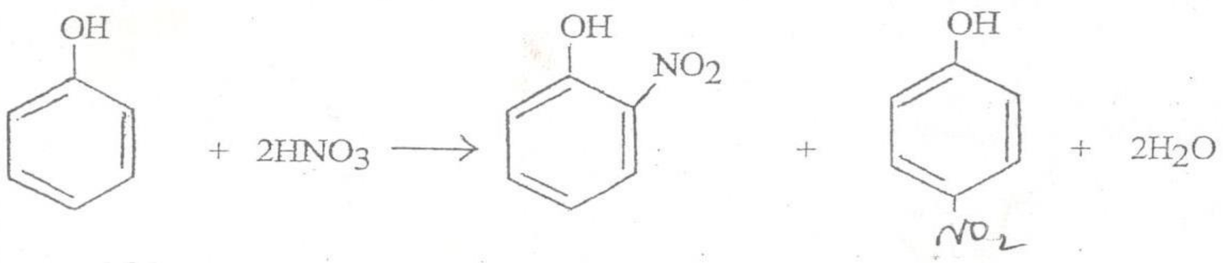


Cyclohexanol

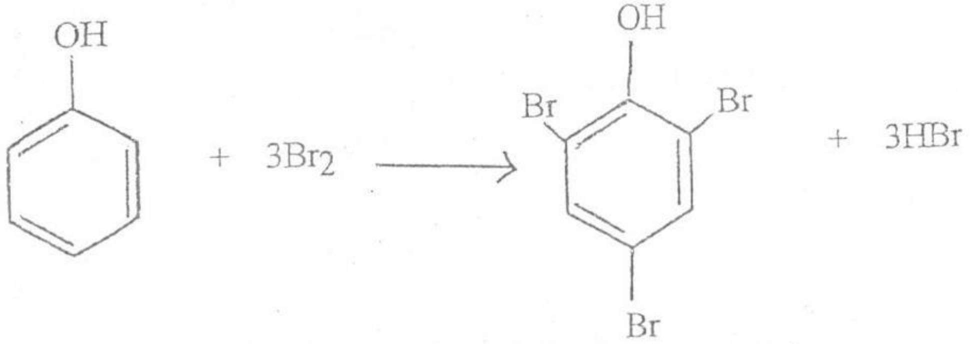
Electrophilic substitution reaction

Phenol is very reactive towards electrophilic reagents. It is more reactive than benzene. The OH group directs the incoming substituents to the *ortho* and *para* positions.

Phenol reacts with dilute nitric acid at room temperature to form *ortho-* and *para* - nitrophenol.



Phenol reacts readily with halogens. An aqueous solution of phenol reacts with bromine water to form a white precipitate of 2,4,6 - tribromophenol.



2,4,6-Tribromophenol

The reaction can be used to test for the presence of phenol and to estimate phenol quantitatively.

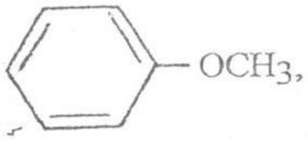
CHAPTER 9

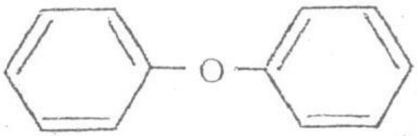
ETHERS

Introduction

Compounds in which oxygen atom is bonded to two alkyl or aryl groups are known as ethers. The alkyl (or the aryl) groups may be the same (simple ethers) or they may be different (mixed ethers).

Examples: CH_3OCH_3, $CH_3OCH_2CH_3$, $CH_3CH_2OCH_2CH_3$,





Nomenclature

Ethers are named as derivatives of hydrocarbons in which the alkoxy (RO) group is regarded as a substituent.

Structures, names and boiling points of some ethers

Structure	*IUPAC Name*	*Common name*	*Bp (^{o}C)*
CH_3OCH_3	Methoxymethane	Dimethyl ether	-24
$CH_3OCH_2CH_3$	Methoxyethane	Ethyl methyl ether	11
$CH_3CH_2OCH_2CH_3$	Ethoxyethane	Diethyl ether	35
$CH_3O(CH_2)_2CH_3$	Methoxypropane	Methyl *n*-propyl ether	39
$CH_3OCH(CH_3)_2$	2 - Methoxypropane	Isopropyl methyl ether	32

Physical properties

The boiling points of ethers are about the same as those of alkanes of corresponding molecular mass but are lower than those isomeric alcohols. This is because molecules of ethers are not associated through hydrogen bonding in the liquid state.

General methods for preparing ethers

1. Simple ethers are formed when an excess alcohol is reacted with concentrated sulphuric acid at about 140° C.

$$2ROH \xrightarrow[\text{heat}]{\text{Conc. } H_2SO_4} ROR$$

$$2CH_3CH_2OH \xrightarrow[140^\circ C]{\text{Conc. } H_2SO_4} CH_3CH_2OCH_2CH_3$$

Williamson's synthesis

Sodium alkoxides react with alkyl halides to form ethers. The method is suitable for the synthesis of both simple and mixed ethers.

$$RX + R'O^- Na^+ \rightarrow ROR' + NaX$$

$$CH_3O^- Na^+ + CH_3CH_2CH_2Br \rightarrow CH_3OCH_2CH_2CH_3 + NaBr$$

Chemical properties of ethers

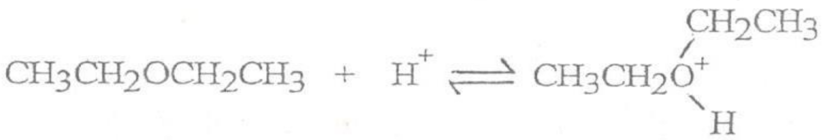
Ethers, like alkanes are rather inert to most reagents.

(a) Combustion

Ethers burn in air to produce carbon dioxide and water. Mixtures with air can be explosive.

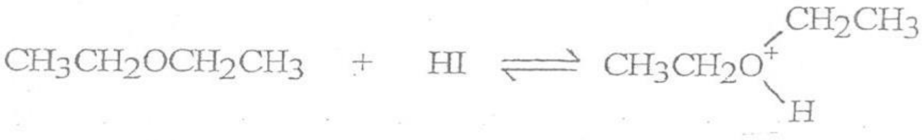
$$CH_3CH_2OCH_2CH_3 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

(b) Ethers dissolve in strong mineral acids. This is because they are protonated by the acids.

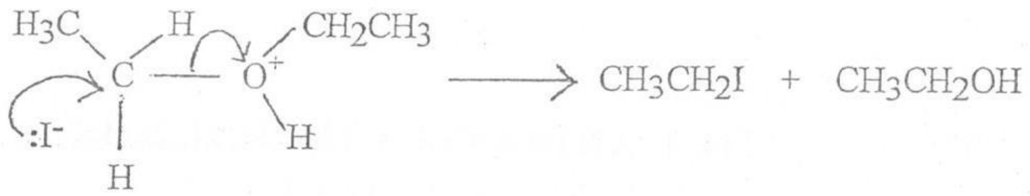


$$CH_3CH_2OCH_2CH_3 + H^+ \rightleftharpoons CH_3CH_2\underset{H}{\overset{CH_2CH_3}{O^+}}$$

When ethers are heated with concentrated hydroiodic acid, alkyl iodides are formed.



$$CH_3CH_2OCH_2CH_3 + HI \rightleftharpoons CH_3CH_2\underset{H}{\overset{CH_2CH_3}{O^+}}$$



(c) Ethers react with phosphorus pentachloride when heated. Hydrogen chloride is not evolved during the reaction since ethers do not contain OH group.

$$ROR' + PCl_5 \longrightarrow RCl + R'Cl + POCl_3$$

CHAPTER 10

THE CARBONYL COMPOUNDS ALDEHYDES AND KETONES

Introduction

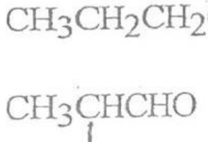
Both aldehydes and ketones contain the structure $C = O$, called the carbonyl group. In the aldehydes the carbon atom of the aldehyde group is bonded to a hydrogen atom while in the ketones the carbonyl carbon is bonded to two carbon atoms. The two classes of compounds show some common properties which are characteristic of the carbonyl group. However, because a hydrogen atom is attached to the carbonyl carbon of the aldehydes, there are some properties shown by aldehydes but not ketones. It is therefore possible to distinguish between the two class of compounds.

Nomenclature

Aldehydes

Aliphatic aldehydes are named by replacing the last e in the name of the corresponding alkane with *al* . The aldehyde group is always at the end of a carbon chain. Hence the carbonyl carbon is assumed to occupy position 1, which is not indicated in the nomenclature.

Examples

HCHO	Methan*al*
CH_3CHO	Ethan*al*
CH_3CH_2CHO	Propan*al*
$CH_3CH_2CH_2CHO$	Butan*al*
 $CH_3CH(CH_3)CHO$	2-Methylpropan*al*

Ketones

In the nomenclature of ketones, the longest continuous chain of carbon atoms containing the carbonyl atom is chosen and numbered to give the carbonyl carbon the lowest possible number. The suffix *one* is then used instead of *ane* in the name of the corresponding alkane.

Examples

CH_3COCH_3	Propan<u>*one*</u>
$CH_3CH_2COCH_3$	Butan<u>*one*</u>
$CH_3CH_2CH_2COCH_3$	Pentan-2-<u>*one*</u>
$CH_3CH_2COCH_2CH_3$	Pentan-3-<u>*one*</u>

General methods for the preparation of aldehydes and ketones

Aliphatic aldehydes

(a) Oxidation of primary alcohols

$$RCH_2OH \xrightarrow{[O]} RCHO$$

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H_2SO_4]{CrO_3} \underset{\text{Butanal}}{CH_3CH_2CH_2CHO}$$

(b) Hydrolysis of gem - dihalides - Hydrolysis of 1,1-dihaloalkanes.

$$RCHCl_2 + 2NaOH \longrightarrow RCHO + 2NaCl + H_2O$$

$$\underset{\substack{\text{1,1-Dichloro-}\\\text{ethane}}}{CH_3CHCl_2} + 2NaOH \longrightarrow \underset{\text{Ethanal}}{CH_3CHO} + 2NaCl + H_2O$$

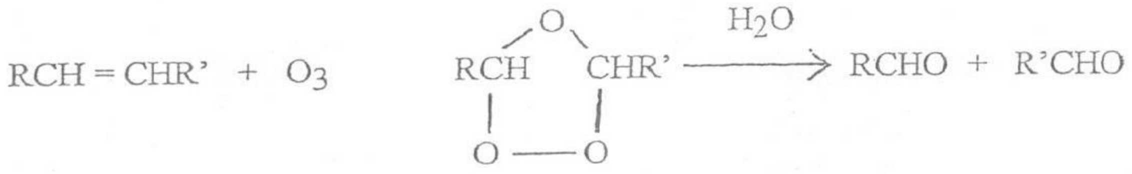
(c) Action of heat on a mixture of calcium salt of a carboxylic acid and calcium formate

$$\begin{matrix} RCO_2^- & & \\ & Ca^{2+} & \\ HCO_2^- & & \end{matrix} \xrightarrow{heat} RHO + CaCO_3$$

$$\begin{matrix} CH_3CO_2^- & & \\ & Ca^{2+} & \\ HCO_2^- & & \end{matrix} \xrightarrow{heat} \underset{\text{Ethanal}}{CH_3CHO} + CaCO_3$$

When calcium methanoate is heated alone, methanal is formed.

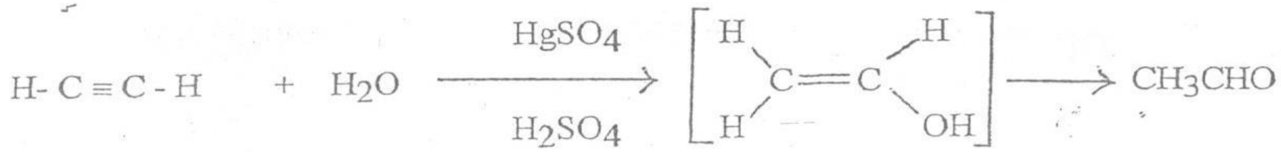
(d) Ozonolysis of alkenes



$$CH_3CH=CHCH_3 \xrightarrow[2)\ Zn/H_2O]{1)\ O_3} 2CH_3CHO$$

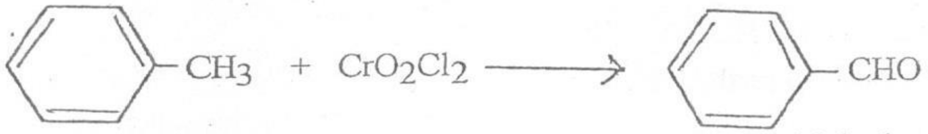
But-2-ene Ethanal

(e) Hydration of ethyne



Aromatic aldehydes

Aromatic aldehydes are obtained when methyl benzenes are oxidised using mild oxidising agents (e.g. chromyl chloride, CrO_2Cl_2). Strong oxidising agents oxidise methylbenzene to benzoic acid.

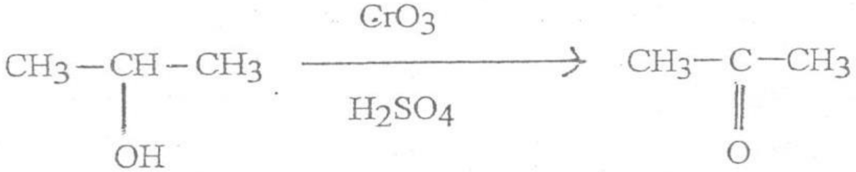


Methylbenzene Benzaldehyde

Aliphatic ketone

(a) Oxidation of secondary alcohols

$$RCH(OH)R' + [O] \longrightarrow RCOR'$$



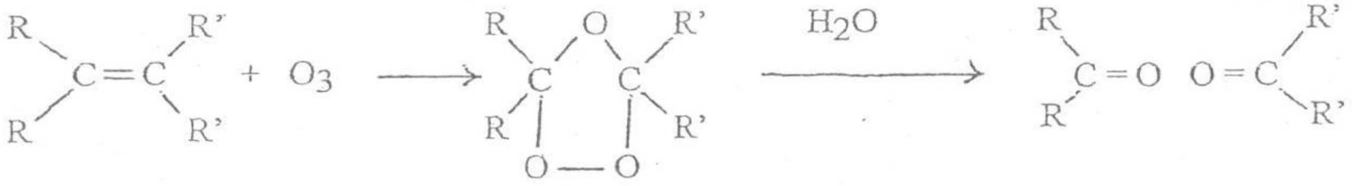
$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow[H_2SO_4]{CrO_3} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

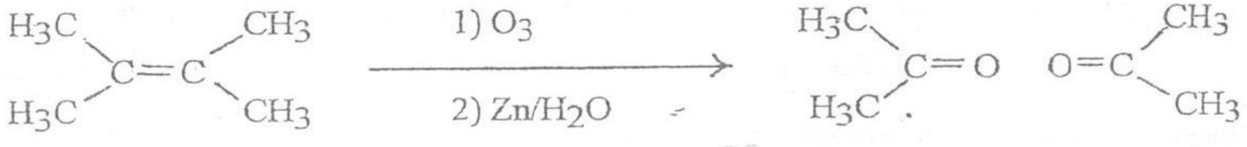
Propan-2-ol Propanone

(b) Hydrolysis of gem-dihaloalkanes

$$RCCl_2R' + 2NaOH \longrightarrow RCOR' + 2NaCl$$

(c) Ozonolysis of alkenes



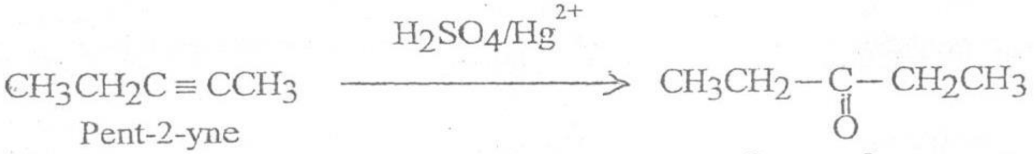


2,3-Dimethylbut-2-ene

Propanone

(d) Hydration of alkynes

$$RC \equiv CR' \xrightarrow{H_2SO_4/Hg^{2+}} RCO.CH_2R'$$



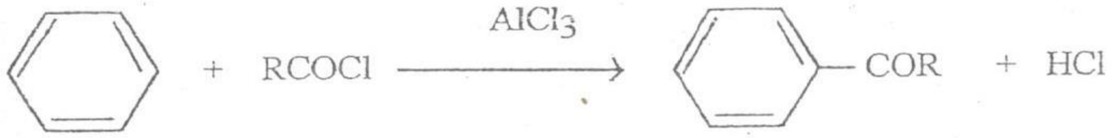
$$CH_3CH_2C \equiv CCH_3 \xrightarrow{H_2SO_4/Hg^{2+}} CH_3CH_2-\underset{\overset{\|}{O}}{C}-CH_2CH_3$$

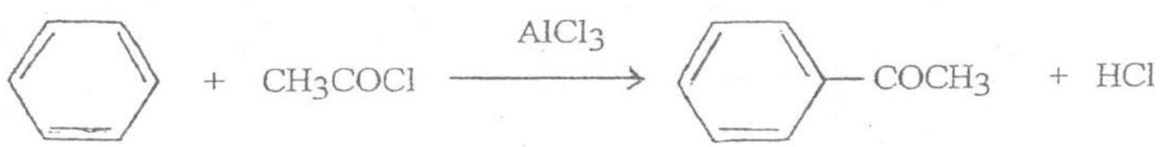
Pent-2-yne

Pentan-3-one

Aromatic ketones

Aromatic ketones are prepared by the Fridel - Crafts acylation reaction.





Acetophenone

Physical Properties of aldehydes and ketones

Boiling points

Methanal is a gas at room temperature. The rest are liquids. Because the carbonyl group is polar, the boiling points of aldehydes and ketones are higher than those of alkanes of similar molecular masses, but are lower than those of the corresponding alcohols since they do not form strong hydrogen bonds with each other.

Solubility

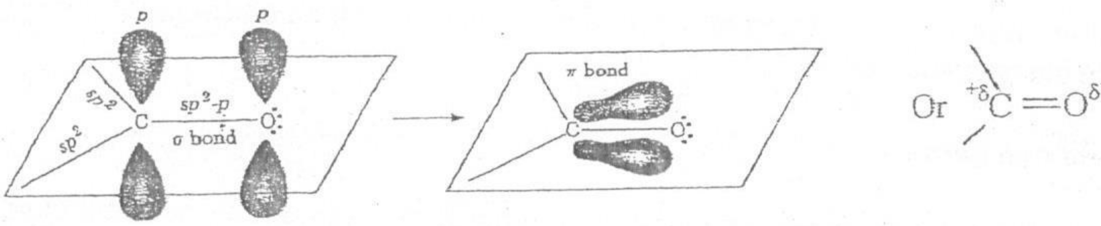
Aldehydes and ketones with low molecular masses are soluble in water. This is because the carbonyl oxygen form hydrogen bonds to water. A 40% solution of methanol in water is called *formalin* and is used as disinfectant. Solubility of aldehydes and ketones in water decreases with increase in molecular mass. Aldehydes and ketones are both soluble in organic solvents.

Physical Properties of aldehydes and ketones

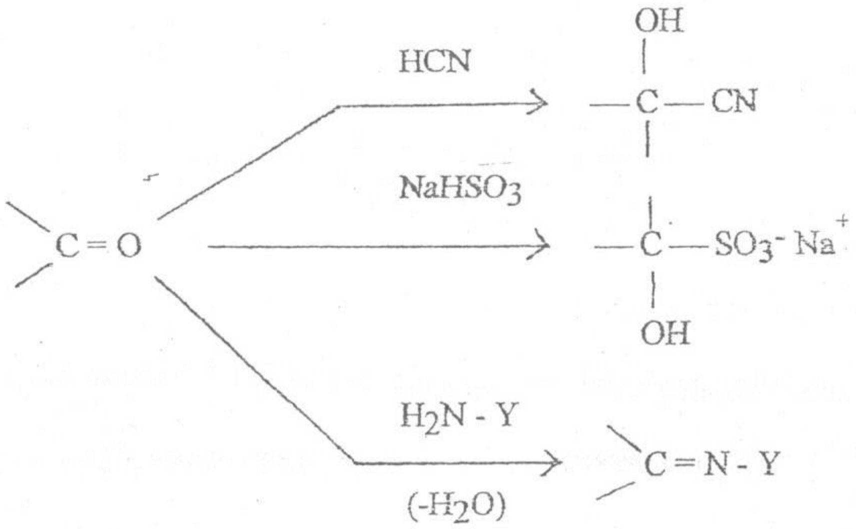
Formula	*Name*	*MP(°C)*	*Bp(°C)*	*Solubility in water*
HCHO	Methanal	-92	-21	Very soluble
CH_3CHO	Ethanal	-125	21	Infinity
CH_3CH_2CHO	Propanal	-81	49	Very soluble
$CH_3(CH_2)_2CHO$	Butanal	-99	76	Soluble
$CH_3(CH_2)_3CHO$	Pentanal	-91.5	102	Slightly soluble
C_6H_5CHO	Benzaldehyde	-51	178	Slightly soluble
CH_3COCH_3	Propanone	-95	56	Infinity
$CH_3COCH_2CH_3$	Butanone	-86	80	Very soluble
$CH_3COCH_2CH_2CH_3$	Pentan-2-one	-78	102	Soluble
$CH_3CH_2COCH_2CH_3$	Pentan-3-one	-39	102	Soluble
$C_6H_5COCH_3$	Acetophenone	21	202	Insoluble
$C_6H_5COC_6H_5$	Benzophenone	48	306	Insoluble

Structure of the carbonyl group

The carbonyl group consists of a carbon to oxygen double bond. The carbonyl carbon is sp^2 hybridised. Thus the three atoms bonded to it lie in the same plane. Oxygen is more electronegative than carbon, hence tends to draw the bonding pair of electrons towards itself. This leaves the carbonyl carbon atom with a partial positive charge and the carbonyl oxygen atom acquires a partial negative charge.



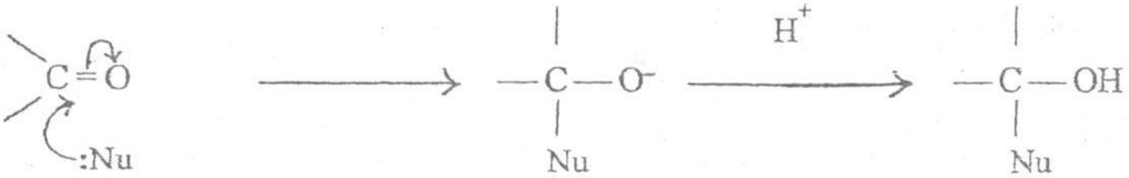
As a result, the carbonyl carbon is subject to nucleophilic attack by a number of nucleophiles. This leads to an addition reaction across the carbon - oxygen double bond. The main reactions of aldehydes and ketones are therefore nucleophilic addition across the carbon - oxygen bond.



Nucleophilic addition to Carbon - oxygen double bond

Nucleophilic addition reaction to the carbonyl double bond can take place in two general ways.

(a) In the presence of a strong nucleophile the reaction can take place as outlined below. The nucleophile attacks the carbonyl carbon atom. At the same time the carbon - oxygen p-bond is cleaved with the electron pair transferred to oxygen which then acquires a negative charge. The negatively charged carbon then reacts with a proton from the solvent to form the product.

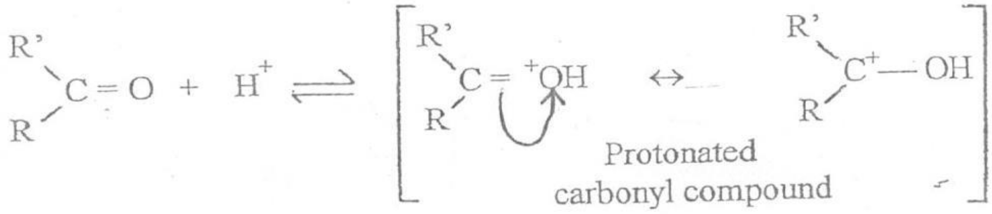


(N = nucleophile)

(b) In the second type of the addition reaction, oxygen reacts with an electrophile (usually a proton) before the addition reaction.

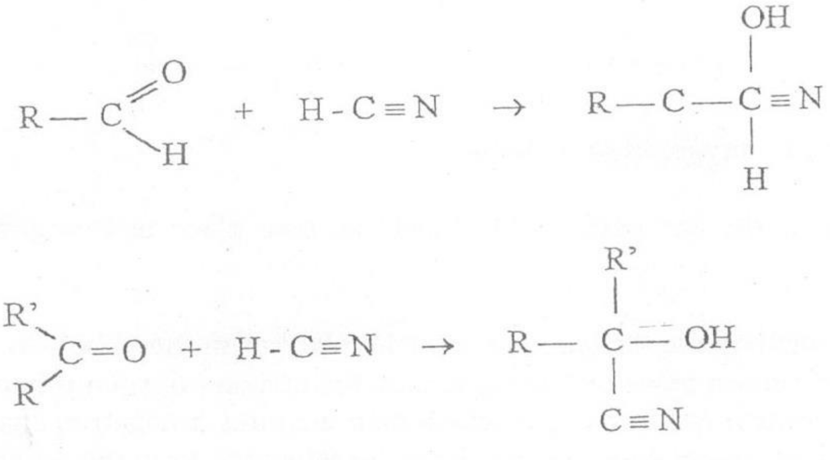
Acid catalysed reactions

The first step in this reaction is the attack by the proton of the acid on the carbonyl oxygen. The resultant protonated carbonyl compound is more reactive towards nucleophilic attack than the unprotonated one. This because of the contribution made by the second resonance structure.



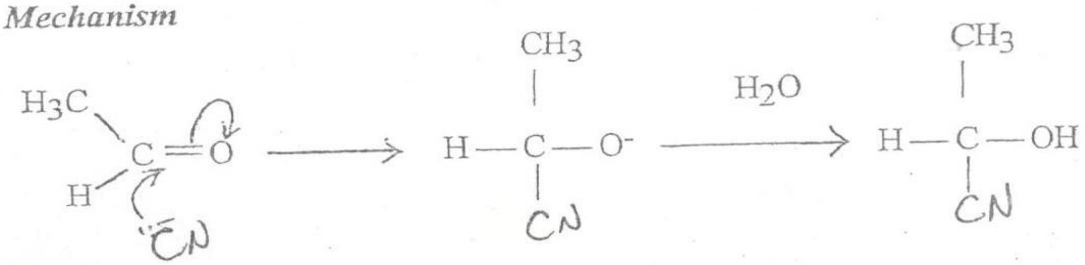
Addition of hydrogen cyanide

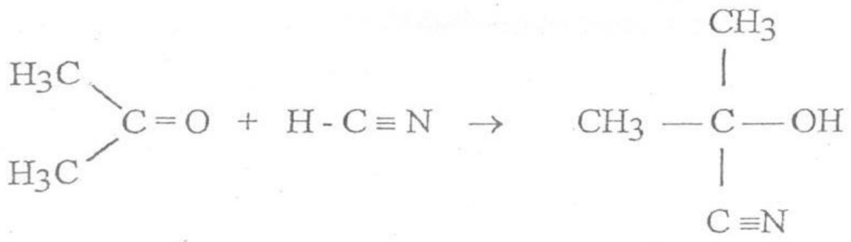
Hydrogen cyanide reacts with aldehydes and most ketones to form cyanohydrins.



Hydrogen cyanide itself is weak acid but the cyanide ion is a strong nucleophile. Normally a solution of alkali metal cyanide in the presence of an alkali is used. Liquid hydrogen cyanide can be used but it is very toxic.

Mechanism



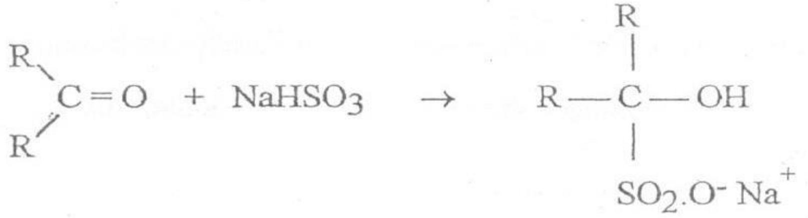


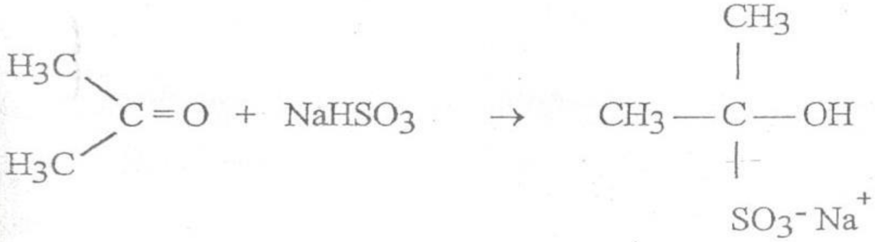
Propanone cyanohydrin

Cyanohydrins are useful intermediates in organic synthesis.

Addition of sodium hydrogen sulphite

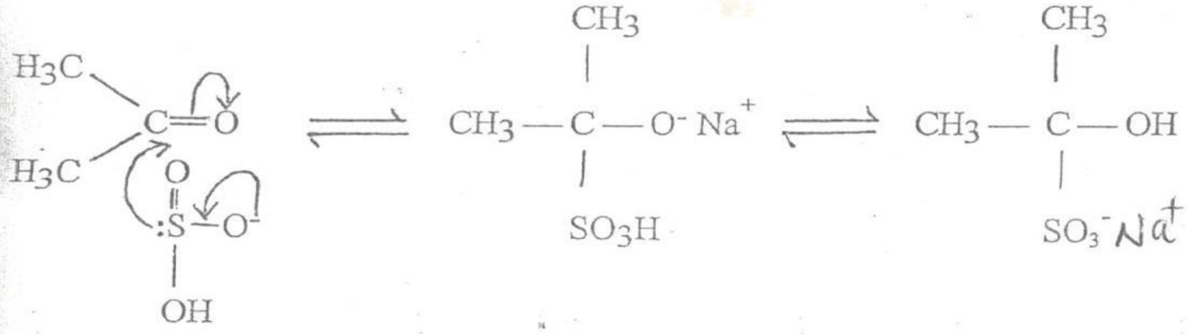
The reaction occur readily with most aldehydes and some ketones (for example methyl ketones).





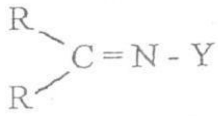
Mechanism

In this reaction, the hydrogen sulphite ion acts as the nucleophile.

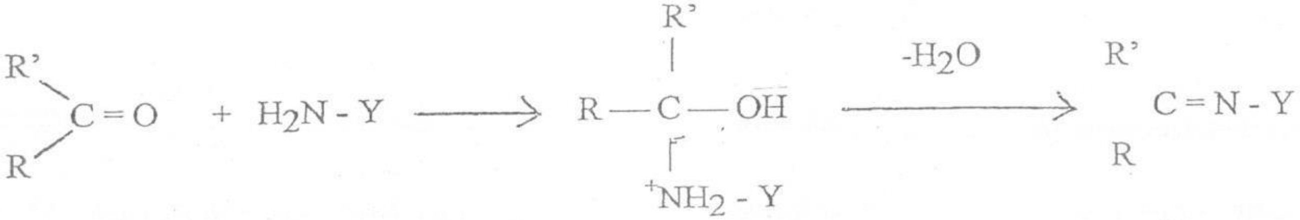


Addition followed by elimination of water molecule (condensation reactions)

A number of compounds with the structure H_2N - Y react with carbonyl compounds to form products which lose a water molecule to give compounds of general structure:

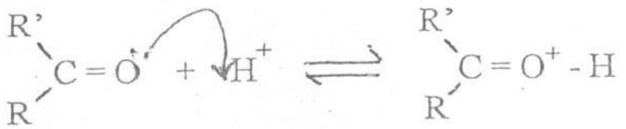


The final products are mostly solids which are used for the characterisation of the starting carbonyl compounds since they are easily isolated and purified by recrystallisation.



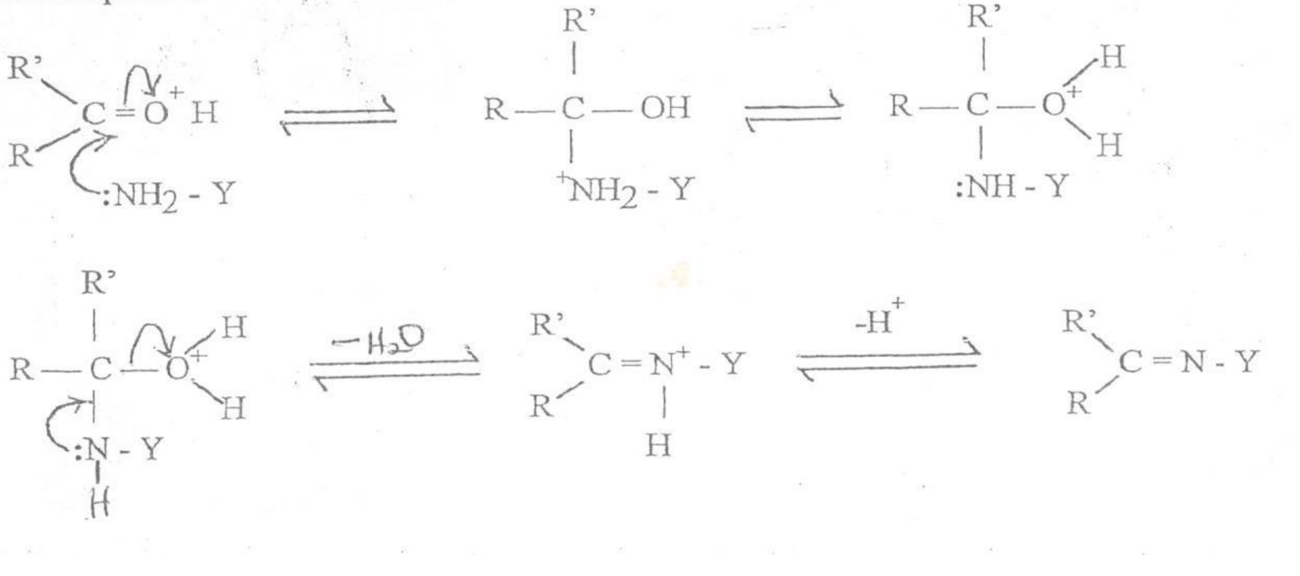
Mechanism

The reaction takes place in the presence of acids, which protonates the carbonyl compound (first step).

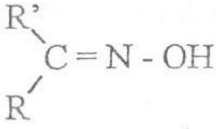
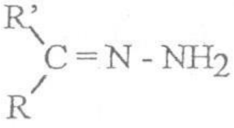
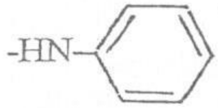
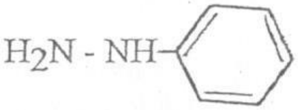
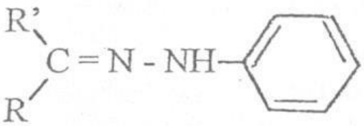
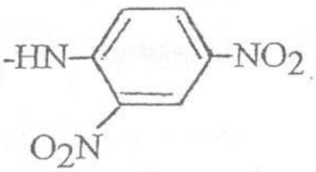
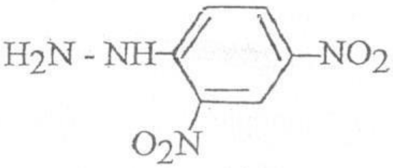
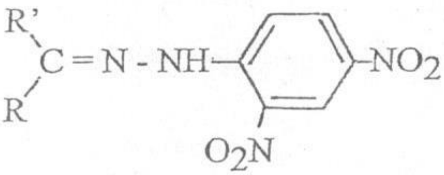


Protonated carbonyl compound

The second step is the nucleophilic attack by Y - NH_2, followed by loss of water molecule then a proton.



Examples

Y	*Reagent*	*Product*
$-OH$	H_2N-OH Hydroxylamine	 Oxime
$-NH_2$	H_2N-NH_2 Hydrazine	 Hydrazone
	 Phenyl hydrazine	 Phenylhydrazone
	 2,4-Dinitrophenylhydrazine (Brady's Reagent)	 2,4-Dinitrophenylhydrazone

Reaction with primary amines

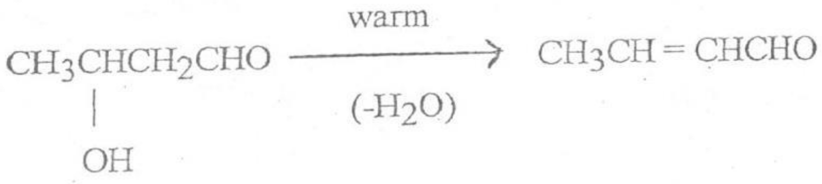
Aldehydes react with primary amines to form ***imines.*** The N-substituted imines are called Schiff's bases.

$$RCHO \quad + \quad H_2NR' \rightarrow \quad RCH=N-R'$$

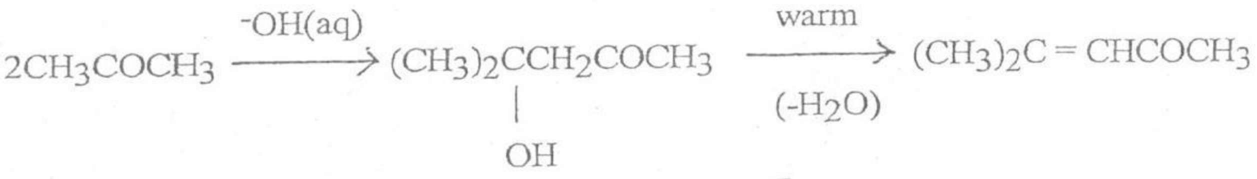
$$CH_3CHO \quad + \quad H_2N-CH_3 \xrightarrow[Na_2SO_4\ (-H_2O)]{\text{ether}} CH_3CH=NCH_3$$

Acetaldehyde (Methanal) + Methylamine (Aminomethane) → Acetaldimine (an imine)

When the solution is warmed, the product loses a water molecule to give an α,β-unsaturated carbonyl compound.



$$CH_3CH(OH)CH_2CHO \xrightarrow[(-H_2O)]{warm} CH_3CH=CHCHO$$

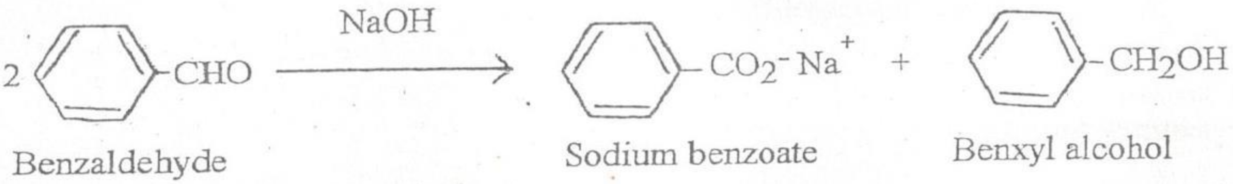


$$2CH_3COCH_3 \xrightarrow{^-OH(aq)} (CH_3)_2C(OH)CH_2COCH_3 \xrightarrow[(-H_2O)]{warm} (CH_3)_2C=CHCOCH_3$$

Cannizzaro reaction

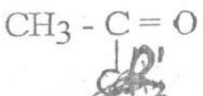
Aldehydes that do not contain an a-hydrogen (e.g. methanal and benzaldehyde) do not undergo the above reaction with alkali instead, they undergo Cannizzaro reaction when reacted with concentrated alkali. The reaction is a self oxidation - reduction of the aldehyde to give the corresponding acid and alcohol.

$$2HCHO + NaOH \rightarrow \underset{\text{Sodium methanoate}}{HCO_2^-\,Na^+} + \underset{\text{Methanol}}{CH_3OH}$$



Haloform reaction

Ethanal and methyl ketones (i.e. carbonyl compounds containing the structure



$$CH_3 - C = O$$

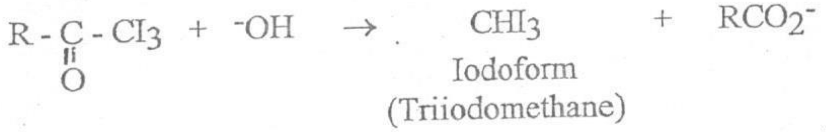
react with halogens in the presence of dilute acids and alkali to form compounds in which one or more of the hydrogen atom(s) has been replaced by the halogen. Chlorine forms chloroform, which is a colourless liquid, bromine forms bromoform as a reddish-brown liquid, while iodine forms a yellow solid iodoform. Since the reaction with iodine in the presence of alkali gives a yellow solid, which is easy to recognise, it is used as a test to identify compounds containing carbonyl carbon bonded to a methyl group and the reaction is known as iodoform test.

Mechanism

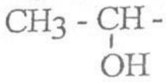
The first step of the reaction involves the replacement of the three hydrogen atoms of the methyl group by the halogen atoms

$$R-\underset{\overset{\|}{O}}{C}-CH_3 + 3I_2 + 3^{-}OH \rightarrow R-\underset{\overset{\|}{O}}{C}-CI_3 + 3I^{-} + 3H_2O$$

In the second step of the reaction the carbon - carbon bond is cleaved by the excess alkali to form triiodomethane (iodoform).



$$R-\underset{\overset{\|}{O}}{C}-CI_3 + {}^{-}OH \rightarrow \underset{\substack{\text{Iodoform}\\ \text{(Triiodomethane)}}}{CHI_3} + RCO_2^{-}$$

Iodine is an oxidising agent and can oxidise alcohols to aldehydes or ketones. Hence alcohols with the structure  $CH_3-\underset{\overset{|}{OH}}{CH}-R$ do also give positive iodoform test.

Ethanol, CH_3CH_2OH is the only primary alcohol with this structure.

Oxidation of aldehydes and ketones

Aldehydes are easily oxidised to the corresponding carboxylic acids whereas ketones are resistant to oxidation by the common oxidising agents. Oxidation under drastic conditions leads to the cleavage of the carbon - carbon bond and are not useful in organic synthesis.

The oxidising agents for aldehydes include:

(a) Powerful oxidising agents e.g. acidified potassium dichromate, acidified chromium trioxide and potassium permanganate.

$$RCHO + [O] \rightarrow RCO_2H$$

(b) Weak oxidising agents. The ready oxidation of aldehydes by these reagents enables the two classes of the carbonyl compounds to be distinguished.

(i) ***Fehlings solutions***

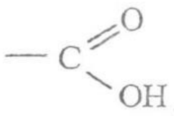
Fehlings solution is an oxidising agent based on the copper(II) ion. It is an alkaline solution of copper(II) tartrate complex ion, obtained by mixing a solution of copper(II) sulphate and a

CHAPTER 11

CARBOXYLIC ACIDS

Introduction

Carboxylic acids are organic compounds that contain the carboxyl group as the functional group. The carbonyl group itself is made up of a carbonyl group and a hydroxyl group.



Carboxyl group

Monocarboxylic acids are monobasic i.e. contain one carboxyl group. Dicarboxylic acids are dibasic.

Nomenclature

The name of a carboxylic acid is systematically derived from that of the corresponding alkane by dropping the ending *e* and adding *oic* acid. The carbon chain is numbered starting with the carbon atom of the carboxyl group as C-1. The position of the carboxyl group is not indicated.

Structure	*Common name*	*I.U.P.A.C. name*
HCO_2H	Formic acid	Methanoic acid
CH_3CO_2H	Acetic acid	Ethanoic acid
$CH_3CH_2CO_2H$	Propionic acid	Propanoic acid
$CH_3CH_2CH_2CO_2H$	Butyric acid	Butanoic acid
$(CH_3)_2CHCO_2H$	*iso* - Butyric acid	2 - Methylpropanoic acid
$CH_3(CH_2)_3CO_2H$	Valeric acid	Pentanoic acid
$CH_3(CH_2)_4CO_2H$	Caproic acid	Hexanoic acid

General methods for the preparation of carboxylic acids

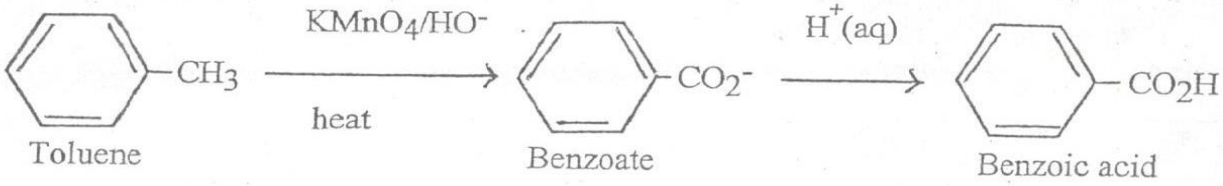
1. Oxidation of primary alcohols or aldehydes with acidified sodium dichromate or acidified chromium trioxide produce carboxylic acids. The oxidising agent in each case is chromic acid, H_2CrO_4, which is formed when chromium trioxide or sodium dichromate is reacted with sulphuric acid.

$$RCH_2OH \xrightarrow[(or\ CrO_3/H^+)]{Na_2Cr_2O_7/H^+} RCHO \xrightarrow[(or\ CrO_3/H^+)]{Na_2Cr_2O_7/H^+} RCO_2H$$

Primary alcohols can also be oxidised to carboxylic acids in basic aqueous solution. Manganese dioxide is precipitated during the reaction. At the end of the oxidation, the precicipated manganese dioxide is filtered off and the filtrate is acidified using a dilute mineral acid to liberate the carboxylic acid which is formed during the reaction as a salt of the acid.

$$\begin{tikzcd}
RCH_2OH + KMnO_4 \arrow[r, "^{-}OH", "H_2O/heat"'] & RCO_2^{-}K^{+} \arrow[d, "H^{+}(aq)"] & + \quad MnO_2 \\
 & RCO_2H &
\end{tikzcd}$$

Alkaline potassium permanganate can also be used to oxidise the methyl group in toluene to a carboxylic acid group.



2. Carboxylic acids are formed when nitriles or amides are heated with dilute mineral acids or alkali.

$$\underset{\text{Nitrile}}{RCN} + H_2O \xrightarrow[\text{heat}]{^{-}OH \text{ or } H^{+}} \underset{\text{Amide}}{RCONH_2}$$

$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow{^{-}OH \text{ or } H^{+}} RCO_2^{-}\,NH_4^{+}$$

$$\begin{tikzcd}
 & RCO_2^{-} + NH_3 + H_2O \arrow[dd, "H^{+}"] \\
RCO_2^{-}\,NH_4^{+} \arrow[ur, "^{-}OH"] \arrow[dr, "HCl"'] & \\
 & RCO_2H + NH_4Cl
\end{tikzcd}$$

Physical properties of carboxylic acids

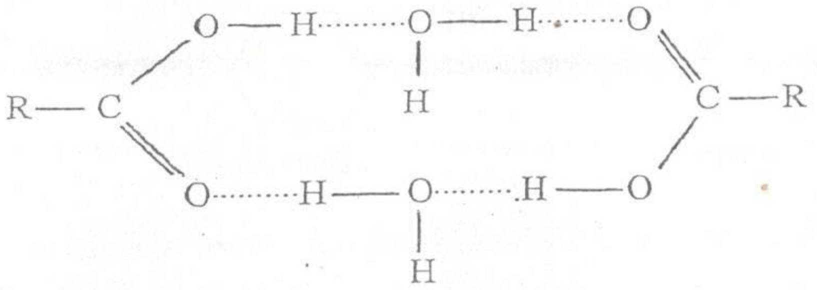
Boiling points and melting points

The boiling points and melting points of carboxylic acids are given in the table below. The boiling points of the acids increase with increase in molecular mass. The lower members are liquids at room temperature whereas long chain acids, e.g. stearic (octadecanoic) acid, are waxy solids. The boiling points of carboxylic acids are higher than expected for their molecular masses. This is because carboxylic acids are polar substances and therefore their molecules are capable of forming hydrogen bonding with each other. Extra energy is thus required to break the hydrogen bonds.

Solubility

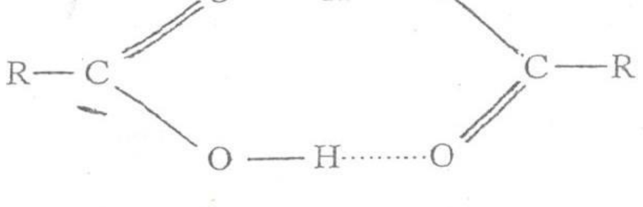
The first four members are miscible with water in all proportions. However, as the chain length is increased, solubility in water decreases.

The solubility in water is due to formation of hydrogen bonds between carboxylic acids and water molecules.



Formation of hydrogen bonds between water carboxylic acid molecules

The formula mass of carboxylic acids determined by for example freezing point method in non - polar solvent (e.g. benzene), is twice the expected value. This is because the molecules of carboxylic acids exist as dimmers through hydrogen bonding in such solvents.



A dimer of a carboxylic acid in a non polar solvent

Melting points, boiling points and solubilities of carboxylic acids

Structure	*Name*	*MP (ºC)*	*Bp(ºC)*	*Solubility in H_2O* *g/100 ml, 20 ºC*
HCO_2H	Methanoic acid	8.4	10	Infinity
CH_3CO_2H	Ethanoic acid	16.6	118	Infinity
$CH_3CH_2CO_2H$	Propanoic acid	-21	141	Infinity
$CH_3(CH_2)_2CO_2H$	Butanoic acid	-5	164	Infinity
$CH_3(CH2)_3CO_2H$	Pentanoic acid	-34	186	4.97
$CH_3(CH_2)_4CO_2H$	Hexanoic acid	-3	205	1.08
$CH_3(CH_2)_5CO_2H$	Heptanoic acid	-8	223	0.24
$CH_3(CH_2)_6CO_2H$	Octanoic acid	17	239	0.07
$CH_3(CH_2)_7CO_2H$	Nonanoic acid	15	255	0.03
$CH_3(CH_2)_8CO_2H$	Decanoic acid	32	270	0.02
$C_6H_5CO_2H$	Benzoic acid	122	250	0.34

Chemical Properties of Carboxylic acids

1. Carboxylic acids are acidic. However, compared to mineral acids, they are weaker acids. This means that they are not completely dissociated in aqueous solutions. They are however, stronger acids than alcohols and phenols. When carboxylic acids are dissolved in water the following equilibrium is set up:

$$RCO_2H + H_2O \rightleftharpoons RCO_2^- + H_3O^+$$

The equilibrium constant for the reaction, K_a, called ***acid dissociation constant*** , can be used to determine the strengths of carboxylic acids. The constant is given by the following expression:

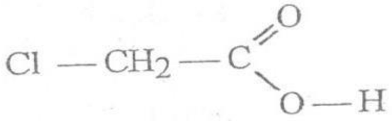
$$K_a = \frac{[RCO_2^-][H^+]}{[RCO_2H]}$$

The square brackets stand for concentrations in moles per litre. The bigger the value of K_a, the stronger is the substance as an acid. The values of some carboxylic acids are given below.

The K_a values of some carboxylic acids

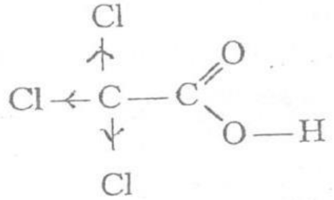
Acid	*K_a at 25^0 C*
HCO_2H	1.7×10^{-4}
CH_3CO_2H	1.7×10^{-5}
$CH_3CH_2CO_2H$	1.3×10^{-5}
$CH_3(CH_2)_2CO_2H$	1.5×10^{-5}
$C_6H_5CO_2H$	6.3×10^{-5}
$C_6H_5CH_2CO_2H$	4.9×10^{-5}

The nature of the groups close to the carboxyl group play great part on the acid strength. The phenomenon is known as ***inductive effect.*** Electron withdrawing groups for example, halogen atoms, nitrile, CN etc., makes the acid stronger. Thus, chloroethanoic acid is a stronger acid than ethanoic acid because of the inductive effect of the chlorine atom and trichloro acid is comparable in strength to mineral acids because of the inductive effect of the three chlorine atoms.



Chloroethanoic acid

(K_a = 1.4×10^{-3})



Trichloroethanoic acid

(K_a = 2.0×10^{-1})

The effect falls off rapidly with increasing distance of the substituent from the carboxyl group. Thus the chlorine atom in $ClCH_2CH_2CO_2H$ has no effect on the strength of the acid.

Electron releasing groups, for example, alkyl groups, on the other hand play the opposite role i.e. they make the acids weaker.

2. Carboxylic acids react with bases to form salts and water.

$$RCO_2H + NaOH \rightarrow RCO_2^- Na^+ + H_2O$$

Carboxylic acids react with carbonates and hydrogen carbonates to liberate carbon dioxide. They are therefore stronger acids than carbonic acid.

$$2RCO_2H + Na_2CO_3 \rightarrow 2RCO_2^- Na^+ + CO_2 + H_2O$$

$$RCO_2H + NaHCO_3 \rightarrow RCO_2^- Na^+ + CO_2 + H_2O$$

Carboxylic acids react with the more electropositive metals such as sodium and magnesium to form salts and hydrogen.

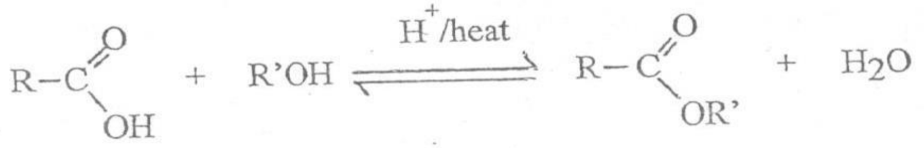
$$2RCO_2H + Mg \rightarrow 2RCO_2^- Mg^{2+} + H_2$$

Cleavage of the C-OH bond

Formation of esters

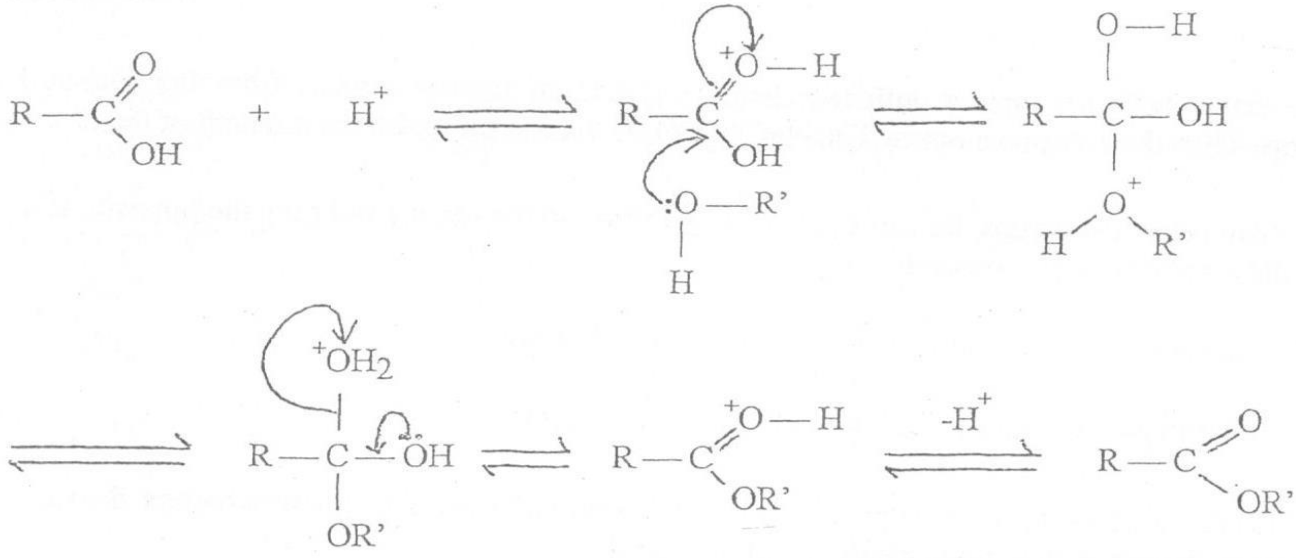
Reaction with alcohols

Carboxylic acids react with alcohols in the presence of mineral acids (e.g. concentrated sulphuric acid) as a catalyst to form esters.



To find out whether the oxygen in the ester came from the acid or from the alcohol, the reaction was studied using a radioactive isotope of oxygen in either the acid or alcohol and analysing the products to find out whether it was in the water or the ester formed. When the oxygen of the alcohol was labelled with a radioactive oxygen and the reaction carried out, the radioactive oxygen was found in the ester and not in the water. This means that during the esterification, it is the C-OH bond of the acid and the O-H bond the alcohol that are cleaved. Hence the mechanism for the reaction was established.

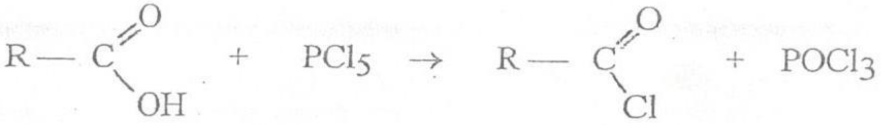
Mechanism



Formation of acid chlorides

(a) Reaction with phosphorus halides

Carboxylic acids react with phosphorus halides to form acid halides.



Reaction with thionyl chloride

Acid chlorides are also formed when carboxylic acids are reacted witht thionyl chloride, $SOCl_2$.

$$RCO_2H + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

Reaction of the alkyl group

When chlorine gas is passed into hot carboxylic acid in the presence of ultraviolet light (or sunlight), one or all the hydrogen atoms bonded to the carbon atom adjacent to the carboxyl group is/are replaced by chlorine atom(s). This is similar to the chlorination of alkane which was discussed earlier.

$$CH_3CO_2H + Cl_2 \xrightarrow[\text{heat}]{\text{u.v. light}} \underset{\substack{\text{Chloroethanoic}\\ \text{acid}}}{ClCH_2CO_2H} + HCl$$

$$ClCH_2CO_2H + Cl_2 \xrightarrow[\text{heat}]{\text{u.v. light}} \underset{\substack{\text{Dichloroethanoic}\\ \text{acid}}}{Cl_2CHCO_2H} + HCl$$

$$Cl_2CHCO_2H + Cl_2 \xrightarrow[\text{heat}]{\text{u.v. light}} \underset{\substack{\text{Trichloroethanoic}\\ \text{acid}}}{Cl_3CO_2H} + HCl$$

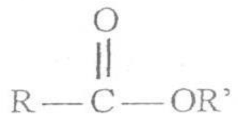
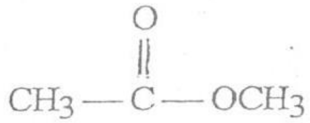
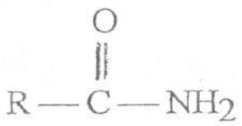
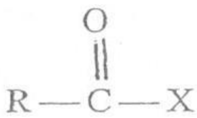
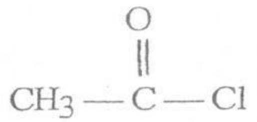
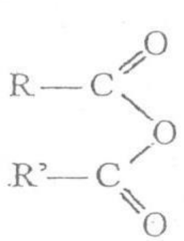
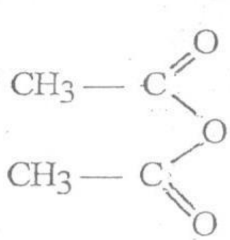
CHAPTER 12

FUNCTIONAL DERIVATIVES OF CARBOXYLIC ACIDS

Introduction

Functional derivatives of carboxylic acids are compounds formed by the replacement of the hydroxyl, OH group of the carboxyl group by another functional group that can be hydrolysed back to the parent acid.

Examples of derivatives of carboxylic acids

Functional group	*General formula of the acid derivative*	*Example*
- OR'	 $R-\overset{\overset{O}{\|}}{C}-OR'$ Ester	 $CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$ Methyl ethanoate
- NH_2	 $R-\overset{\overset{O}{\|}}{C}-NH_2$ Amide	 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ Ethanamide
X (X = Cl, Br or I)	 $R-\overset{\overset{O}{\|}}{C}-X$ Acid halide	 $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ Ethanoyl chloride
- OCOR'	 Acid anhydride .	 Ethanoic anhydride

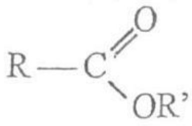
According to the above definition, nitriles are also derivatives of carboxylic acids since they can be hydrolysed to the parent carboxylic acids.

$$RC\equiv N \xrightarrow{H^{+}(aq)\ [or\ ^{-}OH(aq)]} RCO_2H$$

ESTERS

Introduction

Esters are derived from carboxylic acids by the replacement of the OH group of the carboxyl group by R'C- group. They have the general formula:

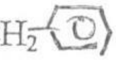
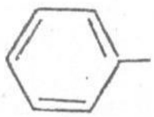


An ester

Nomenclature of esters

In their nomenclature, esters are regarded as if they are formed from carboxylic acids by the replacement of the carboxyl hydrogen by an alkyl group. The alkyl group is named first followed by the name of the parent acid with the ending *-ate* instead of *-ic acid*.

Examples:

Ester	*IUPAC name*	*Common name*
HCO_2CH_3	Methyl methanoate	Methyl formate
$CH_3CO_2CH_2CH_3$	Methyl ethanoate	Ethyl acetate
$CH_3CO_2CH_2$– 	Benzyl ethanoate	Benzyl acetate
 $-CO_2CH_3$	Methyl benzoate	
$CH_3CH_2CH_2CO_2CH_2CH_3$	Ethyl butanoate	Ethyl n-butyrate

Physical properties of esters

Esters are liquids with pleasant fruity smell. They are soluble in organic solvents but are insoluble in water. The boiling points of esters are lower than those of the corresponding carboxylic acids with similar molecular masses. This is because the molecules of esters are not joined together by hydrogen - bonding.

Preparation of esters

1. Esters are prepared by reacting an alcohol with

(a) an acid chloride

$$RCOCl + R'OH \rightarrow RCO_2R' + HCl$$

(b) an acid anhydride

$$(RCO)_2O + R'OH \rightarrow RCO_2R' + RCO_2H$$

2. Esters can also be prepared by reacting alcohols with carboxylic acids in the presence of a mineral acid , e.g. concentrated sulphuric acid.

$$RCO_2H + R'OH \xrightleftharpoons{H^+} RCO_2R' + H_2O$$

Chemical Properties of Esters

1. The most important reaction of esters is hydrolysis i.e. cleavage with water to produce a carboxylic acid and an alcohol.

The hydrolysis can be brought about by the ester with water in the presence of a mineral acid as a catalyst.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightleftharpoons{H^+} CH_3CO_2H + CH_3CH_2OH$$

The reaction is the reverse of the acid catalysed esterification of alcohols.

The hydrolysis of esters can also be brought about by heating the ester with sodium hydroxide solution. The carboxylic acid formed reacts with the alkali to form the salt of the acid thus making the reaction essentially irreversible. The use of a base is therefore more effective for complete hydrolysis of esters.

$$RCO_2R' + Na^+OH^-(aq) \rightarrow RCO_2^-Na^+ + R'OH$$

On reacting with a mineral acid, the salt forms the carboxylic acid which was part of the ester.

$$\mathrm{RCO_2^-Na^+ + H^+(aq) \rightarrow RCO_2H + Na^+(aq)}$$

$$\underset{\text{Ethyl ethanoate}}{\mathrm{CH_3CO_2CH_2CH_3}} + \mathrm{Na^+OH^-(aq)} \rightarrow \underset{\text{Sodium ethanoate}}{\mathrm{CH_3CO_2^-\,Na^+}} + \underset{\text{Ethanol}}{\mathrm{HOCH_2CH_3}}$$

$$\mathrm{CH_3CO_2^-\,Na^+ + H^+(aq)} \rightarrow \underset{\text{Ethanoic acid}}{\mathrm{CH_3CO_2H}} + \mathrm{Na^+(aq)}$$

The hydrolysis of esters using alkali is known as ***saponification reaction*** and is discussed further under fats and oils.

Reduction of esters

Esters are reduced by lithium aluminium hydride to alcohols. The reaction takes place in the presence of sodium dried ether (wet ether reacts with lithium aluminium hydride.

$$\mathrm{RCO_2R'} \xrightarrow[\text{(2) } \mathrm{H_2O}]{\text{(1) } \mathrm{LiAlH_4/ether}} \mathrm{RCH_2OH + R'OH}$$

Reaction of esters with ammonia

Esters react with ammonia to form amides.

$$\mathrm{RCO_2R'} \xrightarrow{\mathrm{NH_3}} \mathrm{RCONH_2 + R'OH}$$

ACID HALIDES

Introduction

Acid halides (also known as acyl halides) are compounds in which the OH group of carboxylic acids is replaced by a halogen atom. They have the general structure:

$$\mathrm{R-\overset{\overset{\displaystyle O}{\|}}{C}-X}$$

(X = Cl, Br or I)

Physical properties of acid halides

Lower members are colourless liquids with pungent smell. They fume in moist air due to hydrolysis.

Boiling points of some acid halides

Name	*Structure*	*B.P. (°C)*
Ethanoyl chloride (acetyl chloride)	CH_3COCl	52
Ethanoyl bromide (acetyl bromide)	CH_3COBr	77
Ethanoyl iodide (acetyl iodide)	CH_3COI	108
Benzoyl chloride	C_6H_5COCl	97

Preparation of acid chlorides

Acid chlorides are prepared from the corresponding carboxylic acids.

Using phosphorus(III) chloride (phosphorus trichloride)

This method is suitable for volatile acid chlorides.

$$3RCO_2H + PCl_3 \rightarrow 3RCOCl + H_3PO_3$$

Using phosphorus(V) chloride (phosphorus pentachloride)

$$RCO_2H + PCl_5 \rightarrow RCOCl + HPOCl_3 + HCl$$

Using thionyl chloride

The by-products this reaction are gases, which makes the method most convenient.

$$RCO_2H + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$

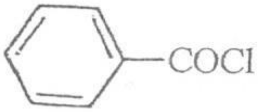
Preparation of acid bromides and acid iodides

Acid bromides are prepared from carboxylic acids using phosphorus tribromide and acid iodides are prepared using a carboxylic acid and phosphorus tri-iodide.

Nomenclature of acid chlorides

Acid chlorides are named by replacing the *-ic acid* in the name of the parent acid by *-yl chloride*.

For example:

Acid chloride	*IUPAC name*	*Common name*
CH_3COCl	Ethanoyl chloride	Acetyl chloride
CH_3CH_2COCl	Propanoyl chloride	Propionyl chloride
$CH_3CH_2CH_2COCl$	Butanoyl chloride	n-Butyryl chloride
	Benzoyl chloride	Benzoyl chloride

Reactions of acid chlorides

Reaction with water

Acid chlorides react vigorously with water to form the parent carboxylic acid and hydrochloric acid.

$$RCOCl + H_2O \rightarrow RCO_2H + HCl$$

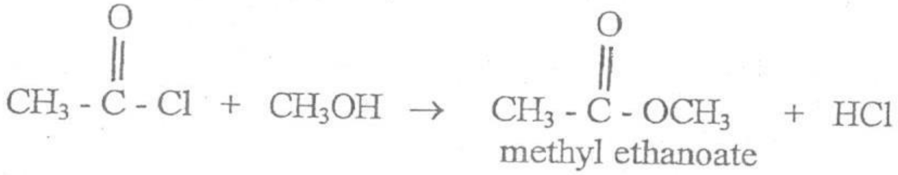
$$CH_3COCl + H_2O \rightarrow CH_3CO_2H + HCl$$

ethanoyl chloride → ethanoic acid

Reaction with alcohols and phenols

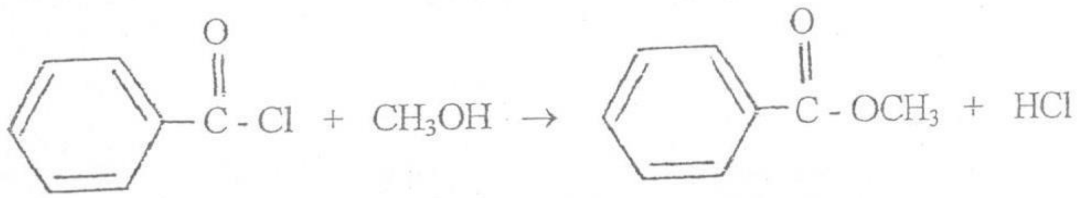
Acid chlorides react with alcohols and phenols to form esters.

$$ROCl + R'OH \rightarrow RCO_2R' + HCl$$



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3OH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + HCl$$

methyl ethanoate

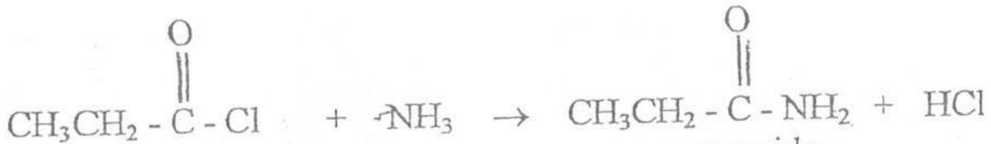


benzoyl chloride methyl benzoate

Reaction with ammonia

Acid chlorides react with ammonia to form unsubstituted (or primary) amides.

$$ROCl + NH_3 \rightarrow RCONH_2 + HCl$$



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-Cl + NH_3 \rightarrow CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + HCl$$

propanoyl chloride propanamide

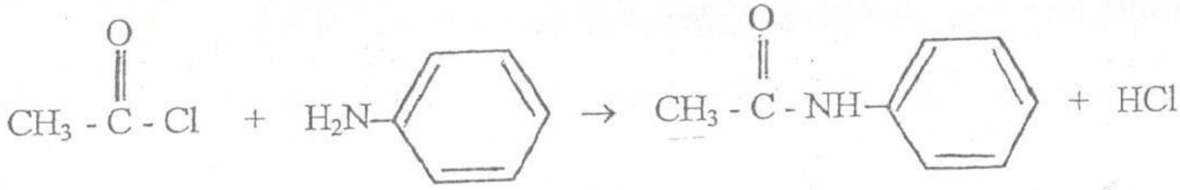
Reaction with amines

N-substituted (secondary) and N,N-disubstituted (tertiary) amides respectively are formed when acid chlorides are reacted with amines.

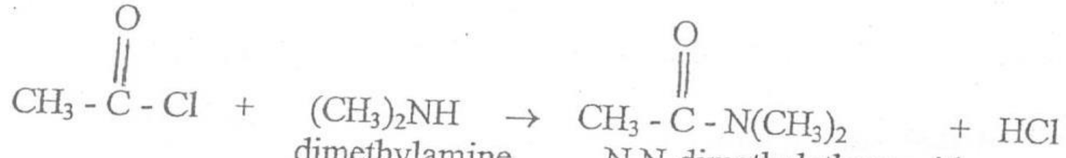
$$\underset{}{RCOCl} + \underset{\text{primary amine}}{R'NH_2} \rightarrow \underset{\text{N-substituted amide}}{RCONHR'} + HCl$$

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3NH_2 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-NHCH_3 + HCl$$

aminomethane N-methylethanamide

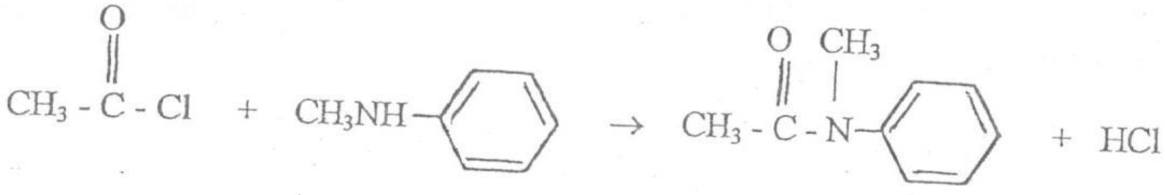


aminobenzene (aniline) acetanilide



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + (CH_3)_2NH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2 + HCl$$

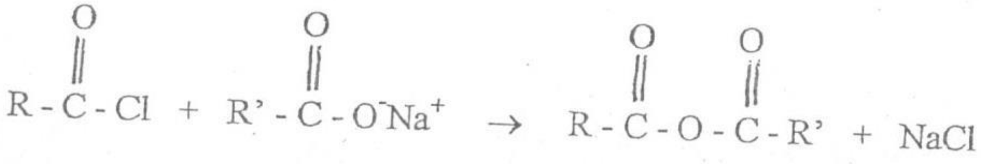
dimethylamine N,N-dimethylethanamide



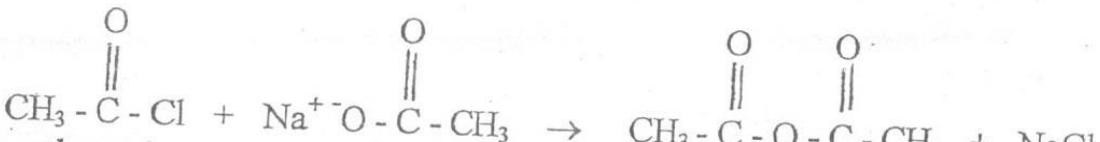
methylaniline N-methylacetanilide

Reaction with sodium salts of carboxylic acids

Acid chlorides react with sodium salts of carboxylic acids to form acid anhydrides.



$$R-\overset{\overset{O}{\|}}{C}-Cl + R'-\overset{\overset{O}{\|}}{C}-O^-Na^+ \rightarrow R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R' + NaCl$$



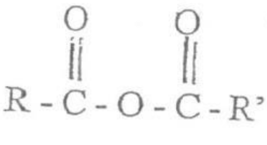
$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + Na^{+-}O-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NaCl$$

ethanoyl chloride sodium ethanoate ethanoic anhydride

ACID ANHYDRIDES

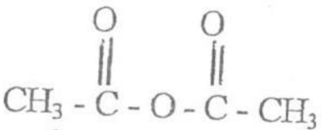
Introduction

Acid anhydrides are compound in which the OH group of carboxylic acids is replaced by the group: -OCOR. They are represented by the general formula:



$$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R'$$

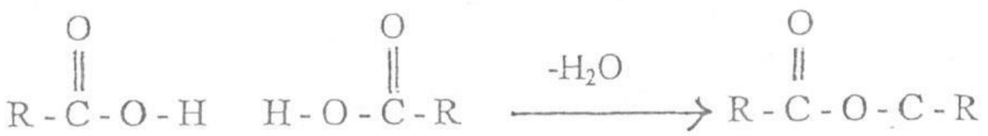
For example,



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

ethanoic anhydride

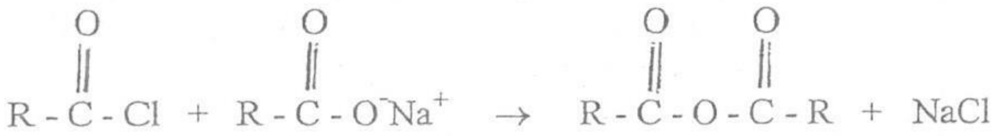
They may be regarded as formed by the loss of a water molecule from two molecules of a carboxylic acid.



$$R-\overset{O}{\overset{\parallel}{C}}-O-H \quad H-O-\overset{O}{\overset{\parallel}{C}}-R \xrightarrow{-H_2O} R-\overset{O}{\overset{\parallel}{C}}-O-C-R$$

Preparation of acid anhydrides

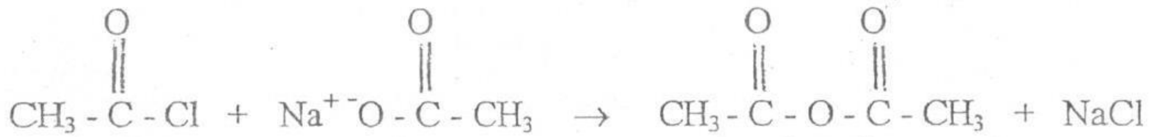
Acid anhydrides are formed when acid chlorides are reacted with anhydrous sodium salts of carboxylic acids.



$$R-\overset{O}{\overset{\parallel}{C}}-Cl + R-\overset{O}{\overset{\parallel}{C}}-O^-Na^+ \rightarrow R-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-R + NaCl$$

$$R-\overset{O}{\overset{\parallel}{C}}-Cl + R'-\overset{O}{\overset{\parallel}{C}}-O^-Na^+ \rightarrow R-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-R' + NaCl$$

'mixed' acid anhydride

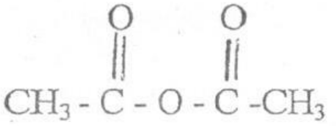
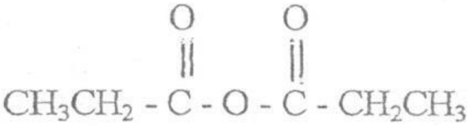


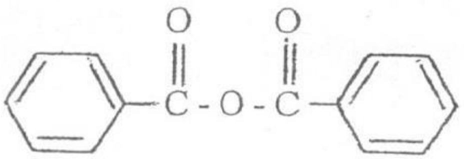
$$CH_3-\overset{O}{\overset{\parallel}{C}}-Cl + Na^{+\,-}O-\overset{O}{\overset{\parallel}{C}}-CH_3 \rightarrow CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3 + NaCl$$

ethanoyl chloride — sodium ethanoate — ethanoic anhydride

Nomenclature of acid anhydrides

In the naming acid anhydrides, the word *acid* in the name of the acid from which it is derived is replaced by *anhydride*.
For example:

Acid anhydride	***IUPAC name***	***Common name***
 $CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$	Ethanoic anhydride	Acetic anhydride
 $CH_3CH_2-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_2CH_3$	Propanoic anhydride	Propionic anhydride

Acid anhydride	*IUPAC name*	*Common name*
	Benzoic anhydride	Benzoic anhydride

Physical properties of acid anhydrides

Lower members are colourless liquids with pungent smells.

Chemical properties of acid anhydrides

Acid anhydrides react with nucleophiles in a similar way to acid chlorides but they are less reactive.

Reaction with water

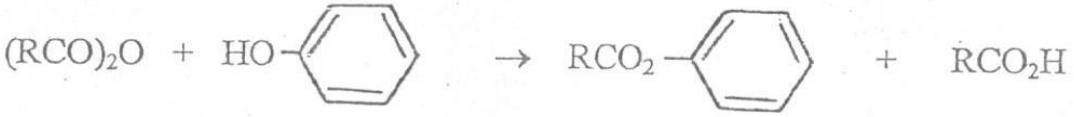
Acid anhydrides react with water to form the parent carboxylic acids.

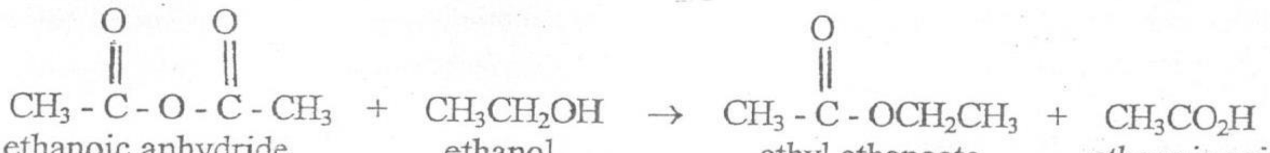
$$(RCO)_2O + H_2O \rightarrow 2RCO_2H$$

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3CO_2H$$

Reaction with alcohols and phenols

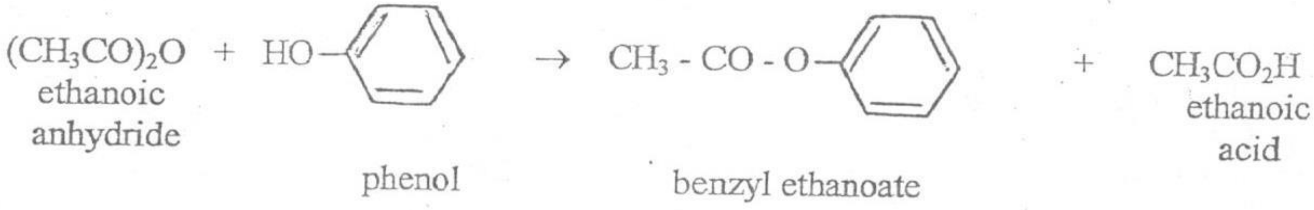
$$(RCO)_2O + R'OH \rightarrow RCO_2R' + RCO_2H$$



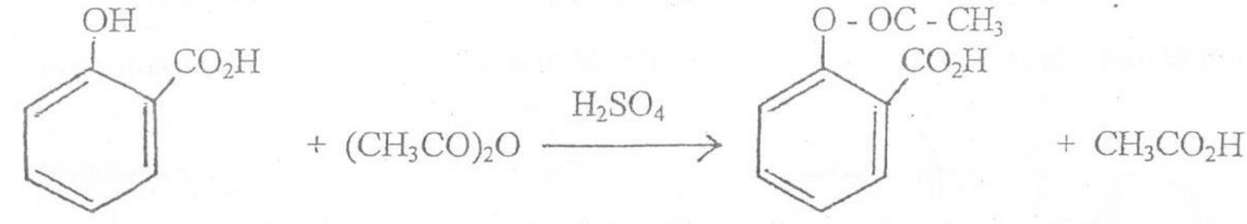


$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3CH_2OH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3 + CH_3CO_2H$$

ethanoic anhydride   ethanol   ethyl ethanoate   ethanoic acid



ethanoic anhydride   phenol   benzyl ethanoate   ethanoic acid

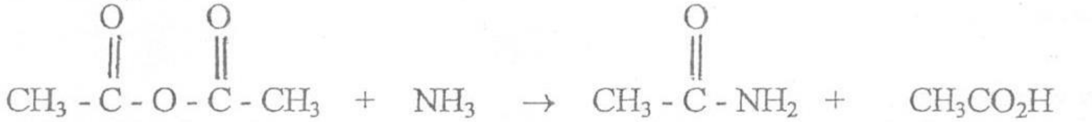


2-hydroxybenzzoic   aspirin

Reaction with concentrated ammonia

Amides are formed when acid anhydrides are reacted with concentrated ammonia solution.

$(RCO)_2O + NH_3 \rightarrow RCONH_2 + RCO_2H$



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NH_3 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3CO_2H$$

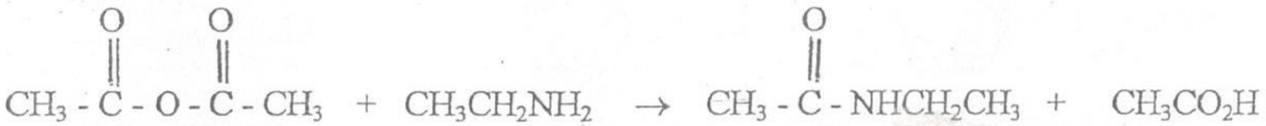
ethanoic anhydride (acetic anhydride) → ethanamide (acetamide) + ethanoic acid (acetic acid)

Reaction with amines

Acid anhydrides react with primary and secondary amines to form N-substituted (secondary) and N,N-substituted (tertiary) amides respectively.

$(RCO)_2O + R'NH_2 \rightarrow RCONHR' + RCO_2H$

primary amine   N-substituted amide



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3CH_2NH_2 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-NHCH_2CH_3 + CH_3CO_2H$$

ethanoic anhydride (acetic anhydride)   N-ethylethanamide (N-ethylacetamide)   ethanoic acid (acetic acid)

$(RCO)_2O + R'R''NH \rightarrow RCONR'R'' + RCO_2H$

secondary amine   N,N-disubstituted amide

$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + (CH_3)_2NH \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2 + CH_3CO_2H$$

ethanoic anhydride   diethylamine   N,N-dimethyl-acetamide   ethanoic acid

AMIDES

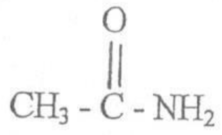
Introduction

Amides are compounds in which the OH of the carboxyl group of carboxylic acids is replaced by an amino group. They can be represented by the following general formulae:

$RCONH_2$	Primary amides (or unsubstituted amides)
RCONHR'	Secondary amides (or N-substituted amides)
RCONR''	Tertiary amides (or N,N-disubstituted amides

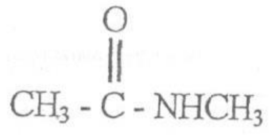
N- and N,N- indicate that the substituents is/are bonded to the nitrogen.

Examples



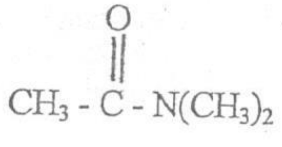
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

Ethanamide (or acetamide)



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NHCH_3$

N-Methylethanamide (or N-methylacetamide)



$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-N(CH_3)_2$

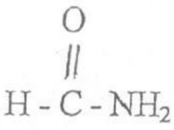
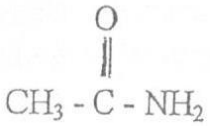
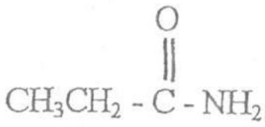
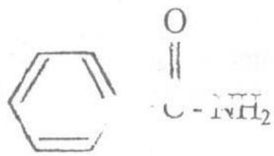
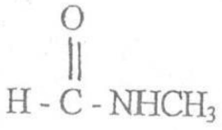
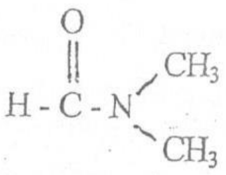
N,N-Dimethylethanamide (or N,N-dimethylacetamide).

General methods for the preparation of amides

Amides are formed when ammonia or amines are reacted with esters (see page 116), acid chlorides (see pages 118 -119) or acid anhydrides (see pages 121-123).

Nomenclature of amides

Amides are named by replacing the *-ioc acid* or *-ic acid* in the name of the parent acid with *-amide*. When there is one or two substituents on the amide nitrogen, the amide is referred to as an N-substituted or an N,N-disubstituted. In this case the substituent(s) is(are) named first. Examples:

Amide	*IUPAC name*	*Common name*
 $H-\overset{\overset{O}{\|}}{C}-NH_2$	Methamide	Formamide
 $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$	Ethanamide	Acetamide
 $CH_3CH_2-\overset{\overset{O}{\|}}{C}-NH_2$	Propanamide	Propionamide
	Benzamide	
 $H-\overset{\overset{O}{\|}}{C}-NHCH_3$	N-Methylmetamide	N-Formamide
	N,N-Dimethylmethamide	N,N-Dimethylformamide

Physical properties of amides

Solubility

Amides with low molecular masses are soluble in water but all amides are soluble in organic solvents.

Boiling points and melting points of amides

The boiling points and melting points of some amides are shown in the table below.

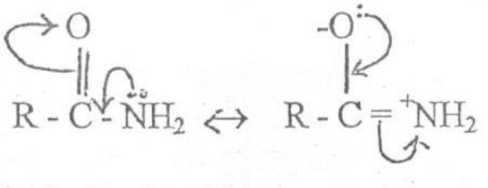
Structure	*Name*	*BP (°C)*	*MP (°C)*
$HCONH_2$	Formamide	193	2.3
$HCONHCH_3$	N-Methylformamide	180-5	-3.8
$HCON(CH_3)_2$	N,N-Dimethylformamide	153	-61
$HCONHCH_2CH_3$	N-Ethylformamide	197-8	...
CH_3CONH_2	Acetamide	82	16.6
$CH_3CONHC_6H_5$	Acetanilide	114	16.6
$CH_3CON(CH_3)C_6H_5$	N-Ethylacetamide	54	249
$CH_3CH_2CONH_2$	Propionamide	79	213
$C_6H_5CONH_2$	Benzamide	130	122

The melting points and boiling points of amides are high because of the hydrogen bonds formed between oxygen atom of one of amide molecule with the hydrogen atom of the amino group of another molecule of amide.

Reactions of amides

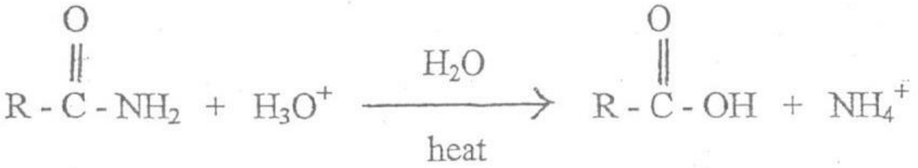
Basic properties of amides

Amides are weaker bases than amines. The lone pair of electrons on the NH_2 of amides is not readily available for donation because it is involved in resonance interaction with the adjacent carbonyl group.



Hydrolysis of amides

Amides are hydrolysed under acidic or basic conditions to the parent carboxylic acids.



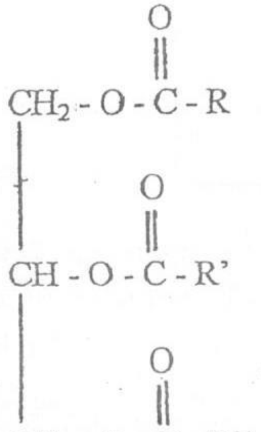
$$R-\overset{O}{\overset{\|}{C}}-NH_2 + H_3O^+ \xrightarrow[heat]{H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_4^+$$

CHAPTER 13

OILS AND FATS

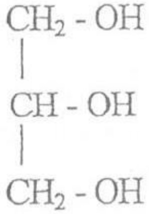
Introduction

Oils and fats are complex mixtures of glycerol with a variety of long-chain carboxylic acids. Fats and oils are similar in chemical structures. Fats are waxy solids at room temperature whereas oils are liquids at the same temperature. The general formula of oils/fats is shown below:



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R'' \end{array}$$

Fat or oil



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array}$$

Glycerol

The acids from which oils and fats are derived have long unbranched chain of carbon atoms. Oils tend to contain greater proportion of unsaturated acids whereas fats tend to contain greater proportion of saturated acids.

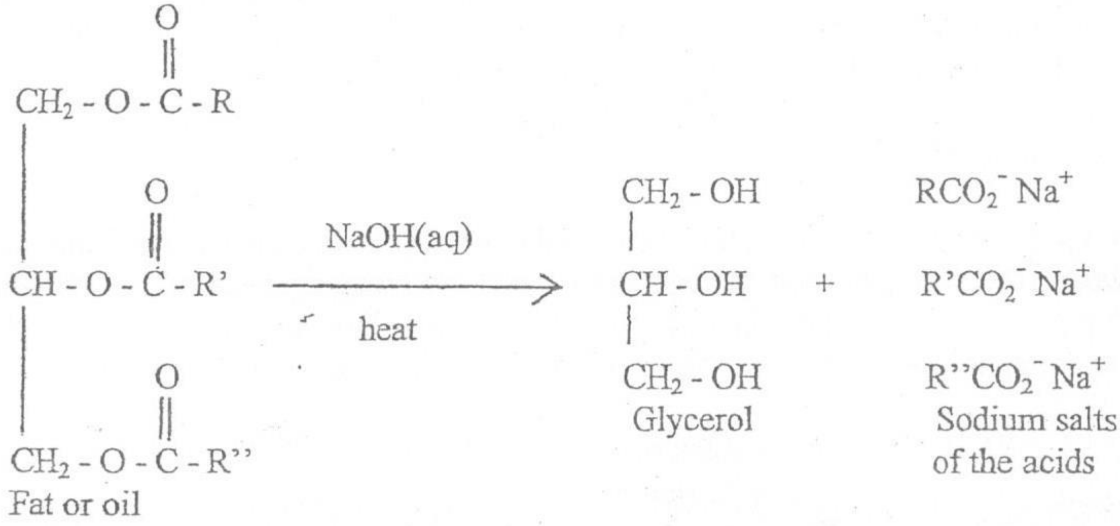
Sources of oils and fats

Vegetable oils and fats are obtained from plant seeds and fruits. For example, cotton seed oil, simsim oil, ground-nut oil, shea butter, palm oil, coconut oil, etc. In the extraction of oil from these sources, the plant material is first cleaned, then heated to break the walls of the oil cells and the oil is expelled by pressing the material. In some cases the heated material is ground and the oil extracted using a suitable solvent, for example hexane. The solvent is then distilled off to leave the oil.

The main source of animal fats are beef, mutton, pork and fish. Fats are generally obtained from these sources by heating the material with water in order to break the fat cells. The fat melts then floats on water.

Saponification of oils and fats

When oils and fats are boiled with aqueous alkali, glycerol and the salts of the carboxylic acids of the oils and fats are formed. This is an example of a hydrolysis reaction. The esters forming the oils and fats are first hydrolysed to form glycerol and carboxylic acids. The latter then react with the excess alkali to form salts. The reaction is known as ***saponification***.



$$\begin{array}{lcccc}
\mathrm{CH_2-O-\overset{\overset{O}{\|}}{C}-R} & & & & \\
| & & \mathrm{CH_2-OH} & & \mathrm{RCO_2^-\,Na^+} \\
\mathrm{CH-O-\overset{\overset{O}{\|}}{C}-R'} & \xrightarrow[\text{heat}]{\text{NaOH(aq)}} & \mathrm{CH-OH} & + & \mathrm{R'CO_2^-\,Na^+} \\
| & & \mathrm{CH_2-OH} & & \mathrm{R''CO_2^-\,Na^+} \\
\mathrm{CH_2-O-\overset{\overset{O}{\|}}{C}-R''} & & \text{Glycerol} & & \text{Sodium salts of the acids} \\
\text{Fat or oil} & & & &
\end{array}$$

The sodium salts of the carboxylic acid are known as ***soap***.

Importance of oils and fats

Oils and fats are important ingredients of a balanced diet. They supply bodily warmth and build physical energy. Thus edible oils and fats are used in cooking or are eaten directly, for example butter and margarine.

In the industries oils are used in making soap, paints, varnishes, as lubricants and plastics. They are also used in cosmetics and pharmaceutical preparations.

The cake left after the oil has been extracted may be used as animal feed or as manure, if poisonous.

Manufacture of soap

In the manufacture of soap, molten fat or heated oil is mixed with sodium hydroxide solution and the mixture boiled for 15 - 24 hours. Brine is then added to precipitate out soap and also to dissolve glycerol. The crude soap is then purified and then blended with perfumes. Dyes may be added to give the soap an attractive appearance.

CHAPTER 14

AMINES

Introduction

Amines may be regarded as derivatives of ammonia obtained by the replacement of one, two or three by alkyl group(s) or by aromatic ring(s). In aliphatic amines, the alkyl groups are bonded directly to the nitrogen atom and in aromatic amines, it is the carbon atom of the aryl (benzene) which is bonded to the nitrogen atom.

Classification of amines

Amines are normally classified according to the number of the alkyl or the benzene rings attached to the nitrogen atom. When there is only one group attached to the nitrogen, it is called a primary amine and when there are two such groups, it is a secondary amine. A tertiary amine is where there are three such groups bonded to the nitrogen atom.

RNH_2	Primary amine
R_2NH	Secondary amine
R_3N	Tertiary amine
$R_4N^+X^-$	Quaternary ammonium salt

Preparation of amines

From alkyl halides

It is possible to prepare amines by reacting alkyl halides with ammonia. However, the method gives a mixture of primary, secondary and tertiary amines as well as quaternary ammonium salt. It is therefore not normally used. In some cases it is possible to separate the mixture by fractional distillation.

$$RCH_2X + NH_3 \rightarrow RCH_2NH_2 + HX$$

$$RCH_2X + RCH_2NH_2 \rightarrow (RCH_2)_2NH + HX$$

$$RCH_2X + (RCH_2)_2NH \rightarrow (RCH_2)_3N + HX$$

$$RCH_2X + (RCH_2)_3N \rightarrow (RCH_2)_4N^+X^-$$

The method cannot be used to prepare aromatic amines because aromatic halides do not react with ammonia under the normal conditions.

Reduction of nitrogen containing compounds

Reduction of nitro compounds

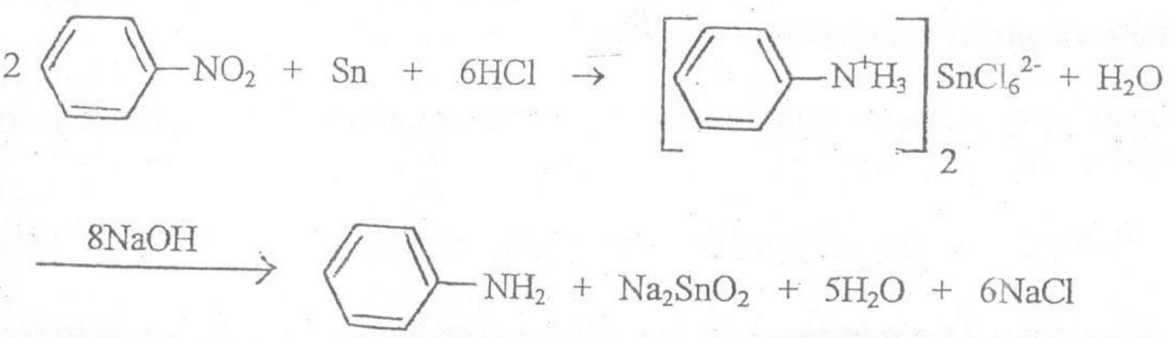
Reduction of nitro compounds give primary amines. The reducing agents that are commonly used include hydrogen gas in the presence of a catalyst (e.g. Raney nickel) or lithium aluminium hydride, $LiAlH_4$.

$$RNO_2 + 3H_2 \xrightarrow{Ni} RNH_2 + 2H_2O$$

$$RNO_2 \xrightarrow{LiAlH_4} RNH_2$$

$$CH_3CH_2NO_2 \xrightarrow{H_2/Pt} CH_3CH_2NH_2$$

In the preparation of aromatic amines, tin and concentrated hydrochloric acid are used for the reduction of aromatic nitro compounds. The amine is formed as a complex salt. Treatment of the salt with alkali liberates the amine.



Reduction of nitriles

Nitriles are reduced to primary amines by lithium aluminium hydride or by hydrogen in the presence of a catalyst.

$$R - C{\equiv}N \xrightarrow{LiAlH_4} RCH_2NH_2$$

$$\underset{\text{butanenitrile}}{CH_3CH_2CH_2 - C{\equiv}N} \xrightarrow{LiAlH_4} \underset{\text{1-aminobutane}}{CH_3CH_2CH_2CH_2NH_2}$$

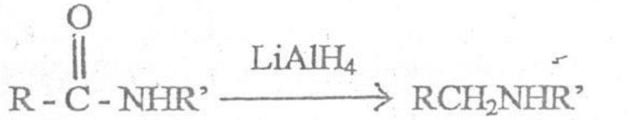
$$\underset{\text{propanenitrile}}{CH_3CH_2-C\equiv N} \xrightarrow{H_2/Pt} \underset{\text{1-aminopropane}}{CH_3CH_2CH_2NH_2}$$

Reduction of amides

Amides are not reduced by hydrogen in the presence of a catalyst. A useful reagent for the reduction is lithium aluminium hydride.

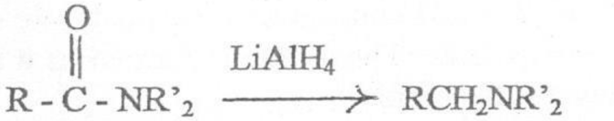
$$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} RCH_2NH_2$$

Primary amide Primary amine



$$R-\overset{\overset{O}{\|}}{C}-NHR' \xrightarrow{LiAlH_4} RCH_2NHR'$$

Secondary amide Secondary amine



$$R-\overset{\overset{O}{\|}}{C}-NR'_2 \xrightarrow{LiAlH_4} RCH_2NR'_2$$

Tertiary amide Tertiary amine

Hofmann degradation of amides

When an amide is heated with bromine in the presence of an alkali, an amine is formed (See page 130).

$$RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

The initial step of the reaction is the reaction between bromine and the amide to form N-bromoamide:

$$RCONH_2 + Br_2 \rightarrow RCONHBr + HBr$$

The N-bromoamide then reacts with the alkali by losing a molecule of hydrogen bromide to form an alkyl isocyanate, $R-N=C=O$.

$$RCONHBr + NaOH \rightarrow R-N=C=O + NaBr + H_2O$$

On heating, ore alkali removes a carbon atom and the oxygen atom from the isocyanate and replaces the with two hydrogen atoms.

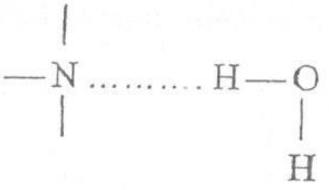
$$R-N=C=O \quad + \quad 2NaOH \quad \rightarrow \quad RNH_2 \quad + \quad Na_2CO_3$$

The amine formed is one carbon atom less than the starting amide. The reaction is therefore used to descending a homologous series. Reduction of amides gives amines with the same number of carbon atoms.

Physical properties of amines

Amines have the smell of rotten fish. Lower molecular mass amines are gases or low boiling liquids at room temperature. Primary and secondary amines posses N - H bonds. Their molecules can therefore form hydrogen bonds of the type H……N. However, the hydrogen bonds are weaker than those in alcohols. This is because nitrogen is less electronegative than oxygen. The boiling points of primary and secondary amines are therefore not as high as those of alcohols of corresponding masses but are higher than those of corresponding alkanes. Tertiary amines do not posses N - H bonds. Molecules of tertiary amines are therefore not associated via hydrogen bonds. Hence they have lower boiling points than primary and secondary amines of comparable masses; but their boiling points are higher than those of alkanes of similar molecular masses.

Lower molecular mass amines are soluble in water. This because their molecules form hydrogen bonds with water molecules.



$$-\overset{|}{\underset{|}{N}}\cdots\cdots\cdots H-\underset{\underset{H}{|}}{O}$$

Comparison of the boiling points of alkanes, amines and alcohols of comparable molecular masses

Structure	*Name*	*Molecular mass*	*BP (°C)*
CH_3CH_3	Ethane	30	-89
CH_3NH_2	Methylamine	31	-7.5
CH_3OH	Methanol	32	64.5
$CH_3CH_2CH_3$	Propane	44	-42
$CH_3CH_2NH_2$	Ethylamine	45	17
CH_3NHCH_3	Dimethylamine	45	7.5
CH_3CH_2OH	Ethanol	46	78

$CH_3CH_2CH_2CH_3$	Butane	58	-0.5
$CH_3CH_2CH_2NH_2$	1-Aminobutane	59	49
$CH_3CH_2NHCH_3$	Methylethylamine	59	35
$(CH_3)_3N$	Trimethylamine	59	3
$CH_3CH_2CH_2OH$	Propan-1-ol	60	97
$CH_3CH(OH)CH_3$	Propan-2-ol	60	82.5

Reactions of amines

Amines as bases

The nitrogen atom of the amines have non-bonded pair of electrons which can be donated to a proton or acid to form an ammonium ion. Amines are therefore bases. They are stronger bases than water and alcohols but are much weaker bases than hydroxide an alkoxide ions. Aqueous solution of amines are therefore weakly basic. This is because amines are only slightly ionised in water.

$$RNH_2 + H_2O \rightleftharpoons RN^+H_3 + {}^-OH$$

The basicity is due to the formation of the hydroxide ion which a strong base.

Since the reaction is reversible, we can write an equilibrium constant, K for the reaction.

$$K = \frac{[RN^+H_3][{}^-OH]}{[RNH_2][H_2O]}$$

Since water is in large excess, its concentration may be regarded as constant and a new equilibrium constant, K_b, can be written as:

$$K_b = K[H_2O] = \frac{[RN^+H_3][{}^-OH]}{[RNH_2]}$$

K_b is known as the ***base dissociation constant***. It is a convenient quantity for comparing the basic strengths of weak bases. A large value of K_b signifies a higher concentration of RN^+H_3 and ^-OH in solution and therefore a strong base. A small value of K_b indicates a weak base i.e. low concentration of RN^+H_3 and ^-OH ions in solution. The value of Kb of some amines together with their boiling points, melting points and their solubilities in water are given in the table below.

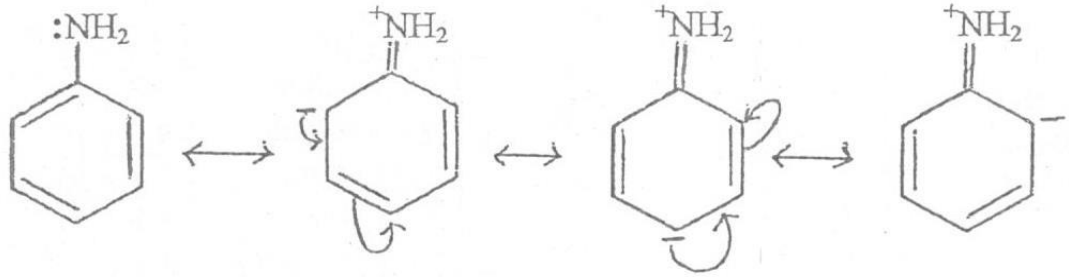
Physical properties of some amines

Structure of amine	*MP (°C)*	*BP (°C)*	*Solubility in water*	*K_b (25 °C)*
Primary amines				
CH_3NH_2	-94	-7.5	Very soluble	4.4×10^{-4}
$CH_3CH_2NH_2$	-84	17	Very soluble	5.6×10^{-4}
$CH_3(CH_2)_2NH_2$	-83	49	Very soluble	4.7×10^{-4}
$(CH_3)_2CHNH_2$	-101	33	Very soluble	5.3×10^{-4}
$CH_3(CH_2)_3NH_2$	-51	78	Very soluble	4.1×10^{-4}
$C_6H_5NH_2$	-6	184	3.7 g per 100 g	3.8×10^{-10}
Secondary amines				
$(CH_3)_2NH$	-96	7.5	Very soluble	5.2×10^{-4}
$(CH_3CH_2)_2NH$	-48	56	Very soluble	9.6×10^{-4}
$C_6H_5NHCH_3$	-57	196	Slightly soluble	5.0×10^{-10}
Tertiary amines				
$(CH_3)_3N$	-117	3	Very soluble	5.2×10^{-4}
$(CH_3CH_2)_3N$	-115	90	14 g per 100 g	5.7×10^{-4}
$C_6H_5N(CH_3)_2$	3	194	Slightly soluble	11.5×10^{-10}

It can be seen from the table of K_b values that the aliphatic amines are stronger bases than ammonia ($K_b = 1.8 \times 10^{-5}$). The basic strength depends on the degree of availability of the non-bonded electrons on the nitrogen to a proton. The more easily available the lone pair of electron is, the stronger is the base and vice versa. Alkyl groups are electron releasing groups. Hence they tend to increase the electron cloud on nitrogen to which they are bonded thus making the non-bonded electrons more available for reaction with protons (acids). They will also stabilise the positive charge on the nitrogen atom in the ammonium ion. Thus primary aliphatic amines are more basic than ammonia and secondary aliphatic amines with two alkyl groups attached to the nitrogen atom are more basic than primary amines. However, in some cases, for example, tertiary aliphatic amines, where there are three alkyl groups are bonded to nitrogen, the non-bonded electrons on the nitrogen atom are not readily available to protons. This is because the alkyl groups are bulky and tend to hinder the approach of the protons to the non-bonded electrons on the nitrogen atom. The amines in such cases are said to be sterically hindered.

The table also reveals that aliphatic amines are stronger bases than aromatic amines. This is because the non-bonded electrons on the nitrogen atom of aromatic amines interact with the π-electron cloud of the benzene ring and are less available for reaction with acids. The non-bonded pair of electron in such cases is not localised (restricted) on the nitrogen atom as is the case with aliphatic amines.

The non-bonded electrons on the aromatic amines are distributed over the nitrogen atom and the benzene ring.



From the canonical structures of aminobenzene above, it can be seen that three of the four structures have a positively charged nitrogen atom and hence do not show basic properties. The true structure of the molecule is a combination of the four structures.

Salt formation

As bases, amines react with acids to form salts.

$$RNH_2 + HX \rightarrow R\text{-}{}^+NH_3X^-$$

$$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2{}^+NH_3Cl^-$$

The salts are soluble in water but insoluble inorganic solvents. Thus amines are soluble in dilute mineral acids. Hence, amines can be separated from non-basic organic compounds by converting them to the salts, for example, using dilute hydrochloric acid. The resulting mixture is then extracted with an organic solvent to remove the non-basic compounds. The aqueous layer on treatment with sodium hydroxide solution liberates the amine, which can then be extracted using an organic solvent.

Since the salts formed are solids, they are also used to store and transport gaseous amines.

Alkylation of amines

Like ammonia, amines react with primary and secondary alkyl halides to form alkylated amines. Complete alkylation leads to the formation of a quaternary ammonium salt

$$RCH_2X + RCH_2NH_2 \rightarrow (RCH_2)_2NH + HX$$

$$RCH_2X + (RCH_2)_2NH \rightarrow (RCH_2)_3N + HX$$

$$RCH_2X + (RCH_2)_3N \rightarrow (RCH_2)_4N^+X^-$$

Amide formation

$$RCOCl + R'NH_2 \rightarrow RCONHR' + HCl$$

primary amine → N-substituted amide

$$R_2NH + R'COCl \rightarrow R'CONR_2 + HCl$$

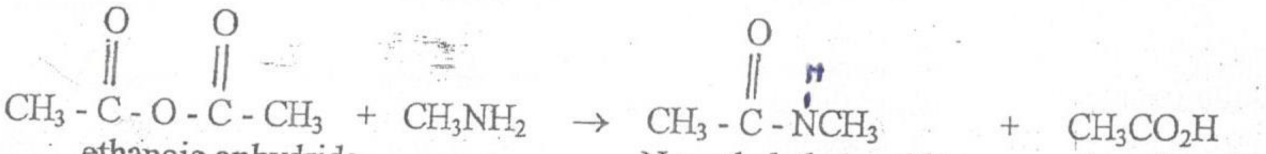
secondary amine → N,N-substituted amid

$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl + CH_3NH_2 \rightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-NHCH_3 + HCl$$

aminomethane → N-methylpropanamide

$$(RCO)_2O + R'NH_2 \rightarrow RCONHR' + RCO_2H$$

primary amine → N-substituted amide



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3NH_2 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{H}{N}CH_3 + CH_3CO_2H$$

ethanoic anhydride (acetic anhydride) → N-methylethanamide (N-methylacetamide) + ethanoic acid (acetic acid)

Tertiary amines do not react.

Reaction with nitrous acid

The product obtained when amines are reacted with nitrous acid depends on whether the amine is primary aliphatic, primary aromatic, secondary or tertiary. The reaction is therefore used to distinguish between the various classes of amines. Nitrous acid itself is unstable at room temperature. It is normally prepared in the reaction mixture (*in situ*) using sodium nitrite, $NaNO_2$, and a mineral acid, for example hydrochloric acid, at low temperatures, 0 - 5 °C.

Reaction with primary aliphatic amines

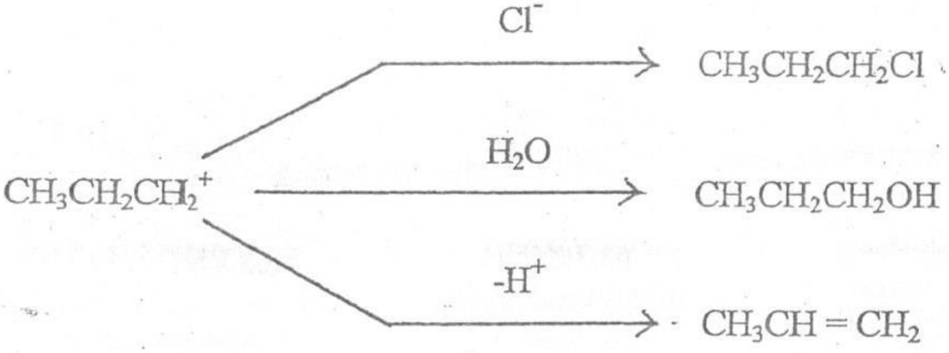
When treated with cold nitrous acid (0 - 5 °C), primary aliphatic amines yield diazonium salts, which decompose to give nitrogen gas (seen as bubbles) and a mixture of products, the main ones being alcohols, alkenes, substitution products and other more complex products.

$$RNH2 + HONO \xrightarrow{HX} \text{(Several intermediates)} \rightarrow [R - N{\equiv}N]^+ X^-$$

$$[R - N{\equiv}N]^+ X^- \rightarrow R^+ + N_2 \xrightarrow{H_2O} \text{Mixture of products}$$

For example:

$$CH_3CH_2CH_2NH_2 \xrightarrow[0\ ^\circ C]{NaNO_2/HCl} [CH_3CH_2CH_2 - N{\equiv}N]^+ Cl^- \rightarrow CH_3CH_2CH_2^+ + N_2$$



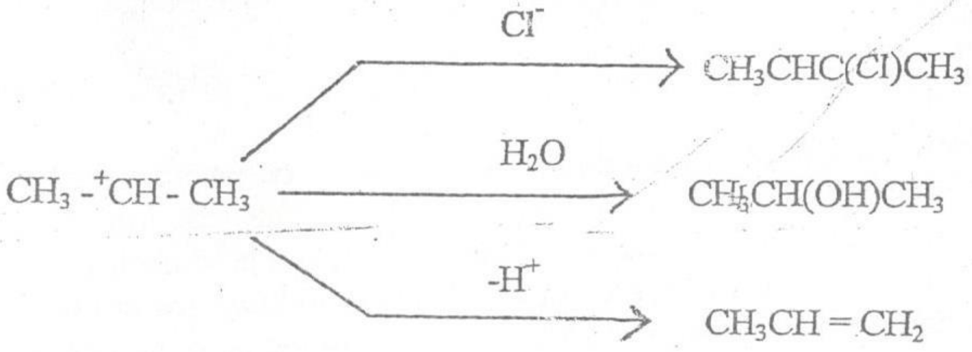
$$CH_3CH_2CH_2^+ \xrightarrow{Cl^-} CH_3CH_2CH_2Cl$$

$$CH_3CH_2CH_2^+ \xrightarrow{H_2O} CH_3CH_2CH_2OH$$

$$CH_3CH_2CH_2^+ \xrightarrow{-H^+} CH_3CH = CH_2$$

The primary carbonium ion formed can rearrange to form the more stable secondary carbonium ion before undergoing the above reactions.

$$\underset{\text{Primary carbonium ion}}{CH_3CH_2CH_2^+} \rightarrow \underset{\text{Secondary carbonium ion}}{CH_3 - {}^+CH - CH_3}$$



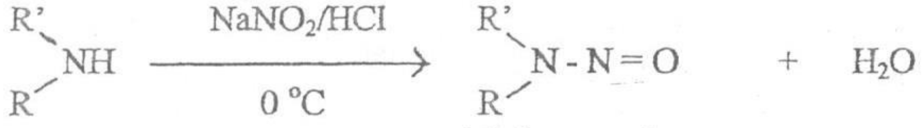
$$CH_3 - {}^+CH - CH_3 \xrightarrow{Cl^-} CH_3CHC(Cl)CH_3$$

$$CH_3 - {}^+CH - CH_3 \xrightarrow{H_2O} CH_3CH(OH)CH_3$$

$$CH_3 - {}^+CH - CH_3 \xrightarrow{-H^+} CH_3CH = CH_2$$

Reaction with secondary amines

Secondary amines (aliphatic and aromatic) react with nitrous acid to form N-nitrosoamines instead of diazonium salts, without the evolution of nitrogen gas. The nitroso compounds so formed are yellow oils. Lower amines form yellow turbid solutions.



N-nitrosoamine

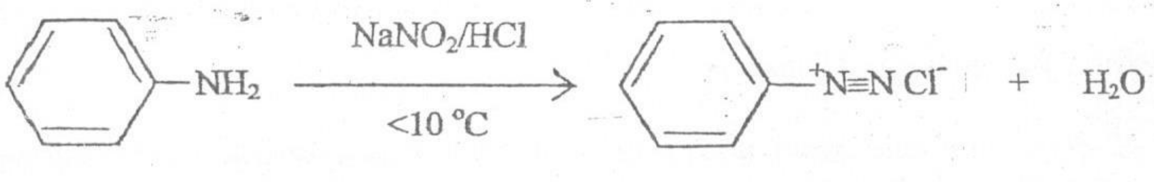
Reaction with tertiary amines

Tertiary amines react with cold nitrous acid to form water soluble salts. Clear solutions are obtained with no eyolution of nitrogen gas.

$$R_3N + HNO_2 \rightarrow R_3 - {}^{+}NH\ NO_2^-$$

Reaction with primary aromatic amines

Primary aromatic amines react with cold nitrous acid to form diazonium salts that are stable in solution below 10 oC. A clear solution is obtained without evolution of nitrogen gas.



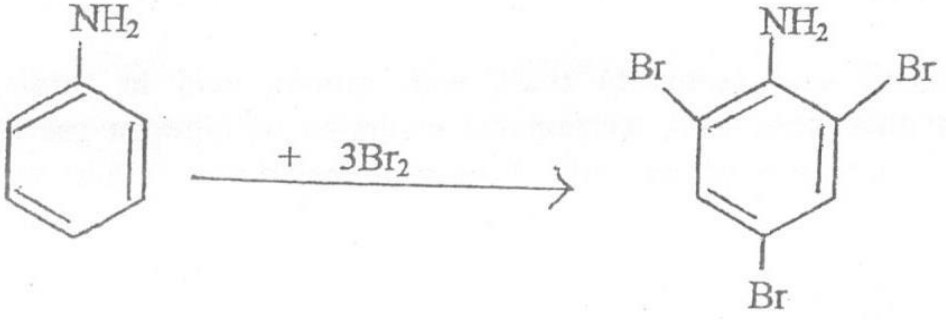
Benzenediazonium chloride

The reaction is known as diazotaasation. Because of their instability, aromatic diazonium salts are not normally isolated from the aqueous solutions in which they are made.

Reactions of aromatic amines - Substitution in the benzene ring

The amino group directs the in coming substituent to the *ortho* (2-) and *para* (4-) positions and activates the benzene ring towards electrophilic substitution reactions.

For example, aniline reacts with bromine water at room temperature to give 2,4,6-tribromoaniline.



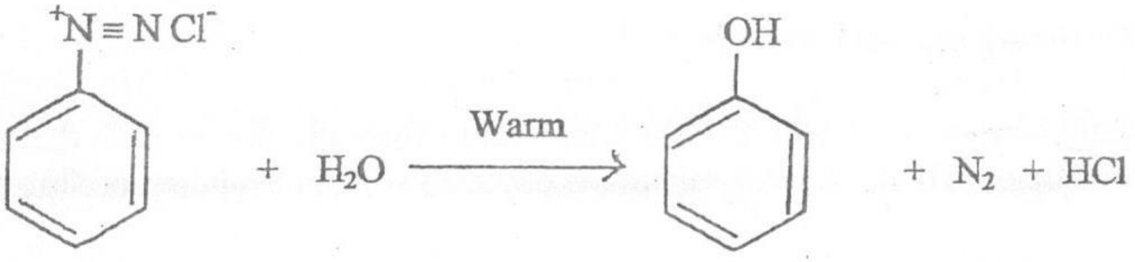
White precipitate

Reactions of benzenediazonium salts

Reactions in which the nitrogen atoms are replaced

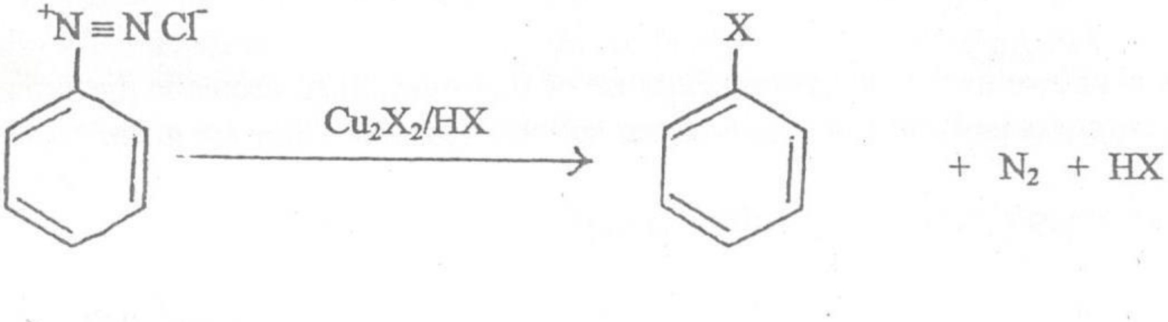
Replacement by the hydroxyl group

When a solution of benzenediazonium salt is warmed, the two nitrogen atoms are lost as nitrogen gas and a phenol is formed as the major product.



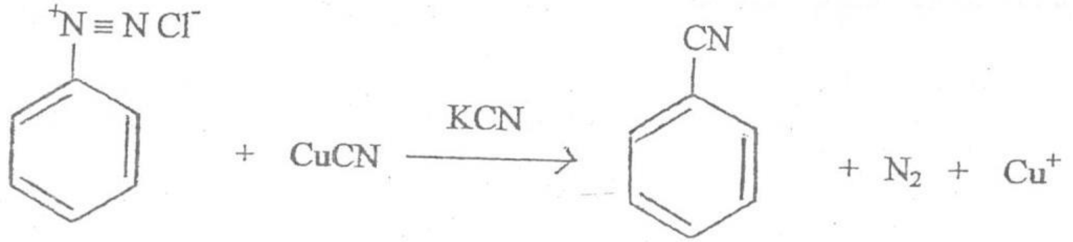
Replacement by chlorine and bromine

Solution of diazonium salts react with a solution of copper(I) halide in concentrated halogen acid to form a halobenzene.



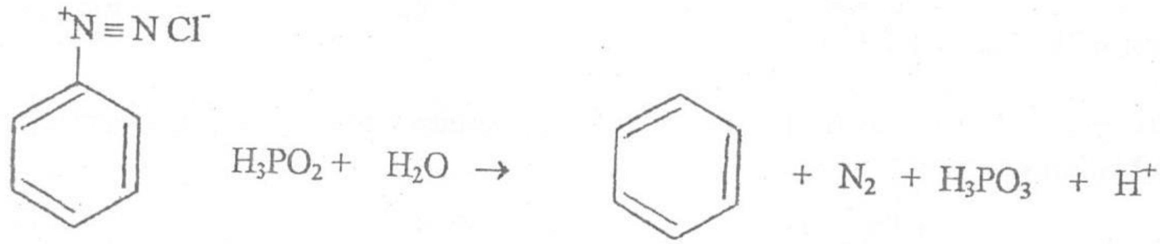
(X = Cl or Br)

Replacement by the nitrile group



Replacement by hydrogen

Solutions of benzenediazonium salts react with excess aqueous hypophosphorus acid to form benzene.

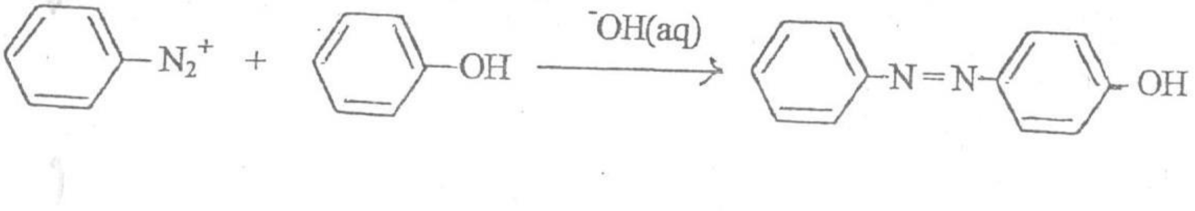


Reactions in which nitrogen is retained

One of the most important industrial uses of aromatic diazonium salts is in the manufacture of ***azo dyes***. When aromatic diazonium salts are reacted with phenols or tertiary aromatic amines, a reaction takes place without the loss of nitrogen atoms. The products are ***azo*** compounds, formed by the coupling of the two aromatic rings. Azo compounds are coloured and belong to a class of compounds known as ***azo dyes***.

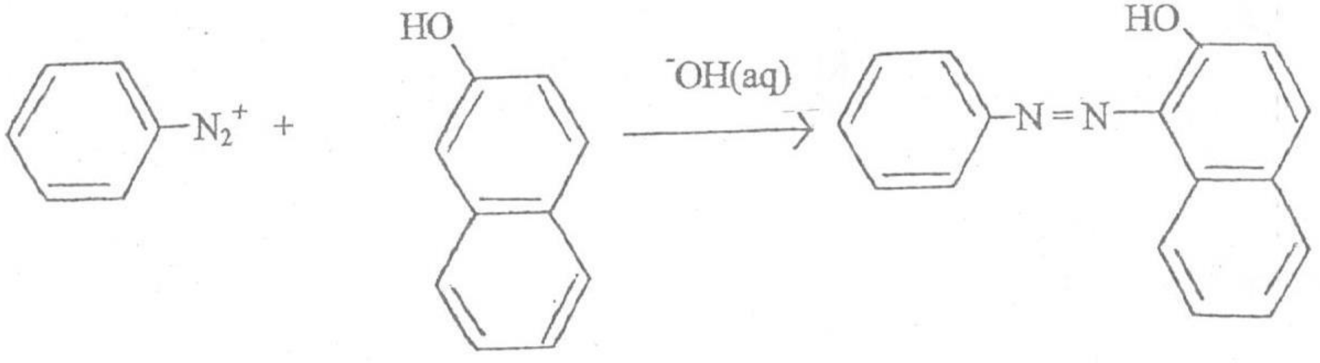
Reaction with phenols

The reaction with phenols is carried out in alkaline solutions.



4-Hydroxyazobenzene
(Orange solid)

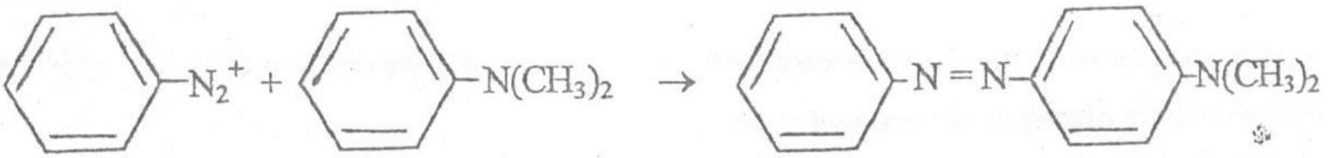
The second reaction similar to the one above is the reaction between benzenediazonium salt and 2-naphthol (β-naphthol). The products formed between 2-naphthol and aromatic diazonium salts are normally red solids and the reaction is used as a test to confirm the presence of a primary aromatic amine.



1-Phenyl-2-azo-naphthol
(Red solid)

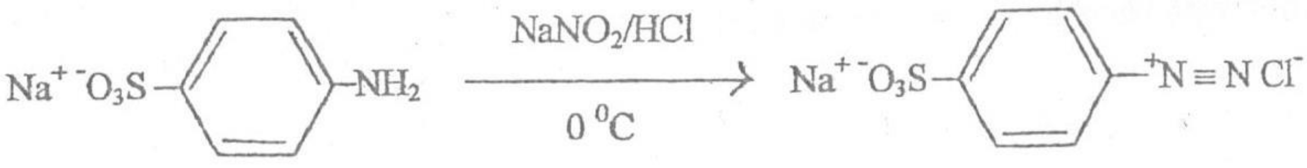
Reactions with amines

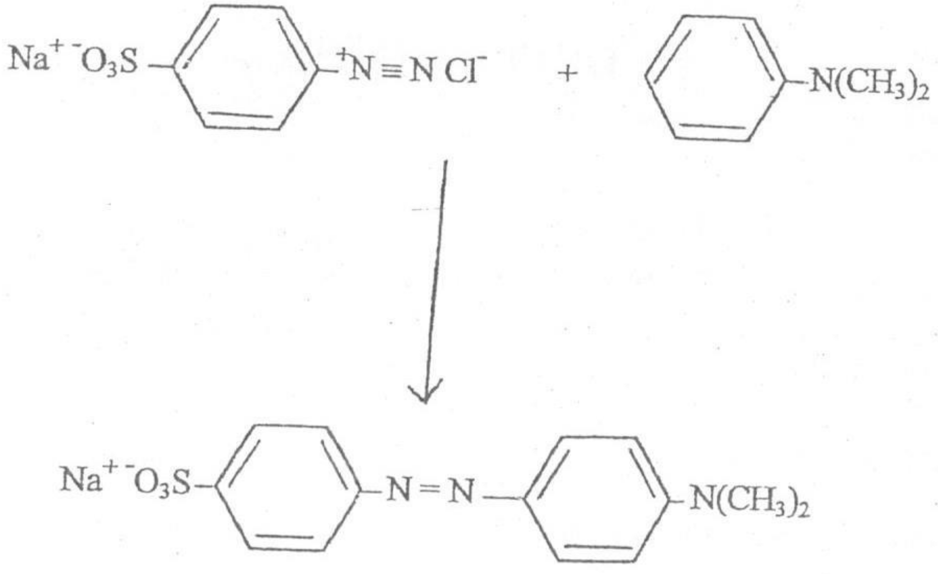
The reaction between aromatic diazonium salts and tertiary aromatic amines takes place in neutral solutions.



4-Dimethylaminoazobenzene
(Yellow solid)

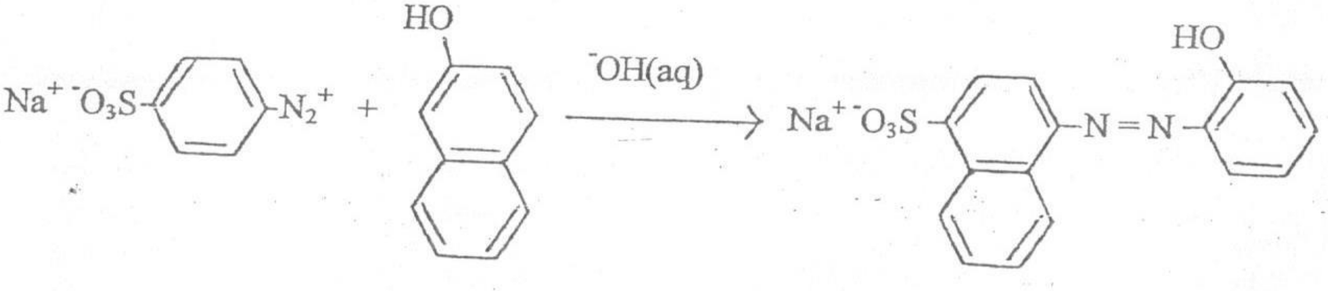
In the diazotisation of sulphanilic acid, the acid is first converted to its sodium salt by reacting it with aqueous sodium carbonate and then sodium nitrite added, followed by a calculated amount of hydrochloric acid to the cold solution.





Methyl orange

Methyl orange is used as an indicator in the acid-base titration. It is red in acid medium and is yellow in a basic medium.



Orange

CHAPTER 15

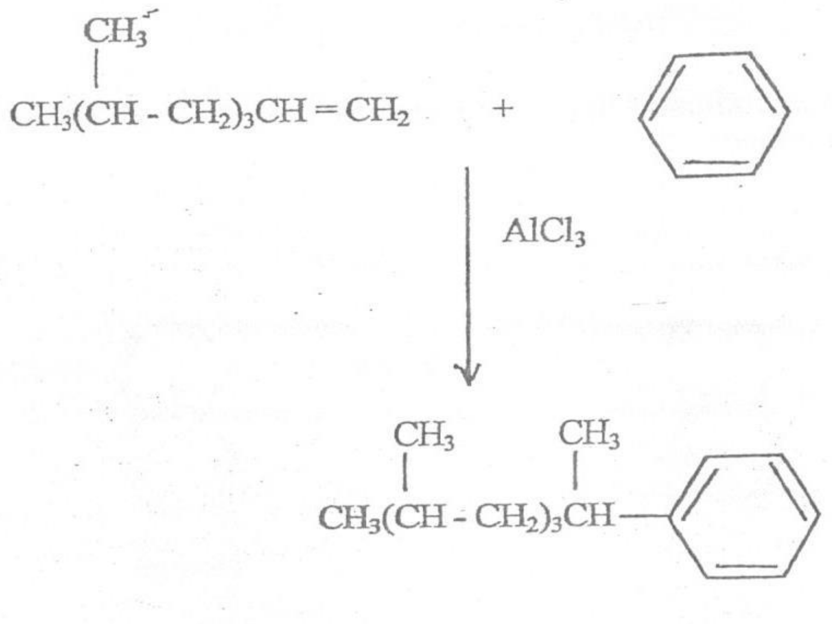
DETERGENTS

Introduction

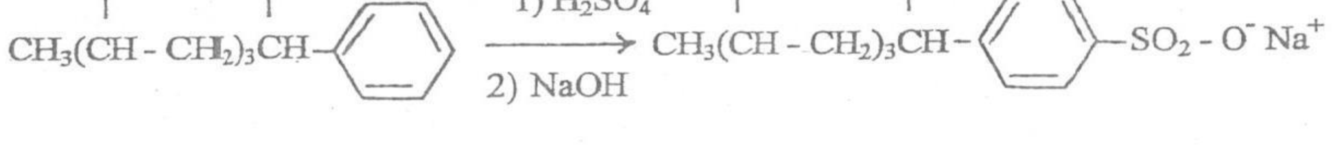
Detergents are substances in which the carboxylate group I the soap is replaced by a sulphonate group, - SO_2 - O^-, or a sulphate group, - O - SO_2 - O^-. They have advantage over soap in that unlike soaps, which form insoluble calcium salts with calcium ions in hard water, they form calcium salts that are soluble in water.

Manufacture of detergents

Originally detergents were manufactured by alkylation of benzene

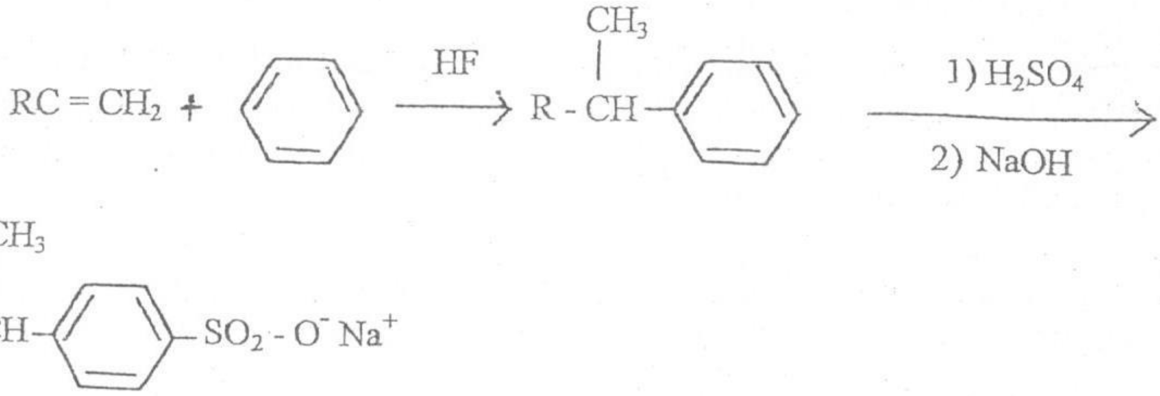


The alkylated benzene is then sulphonated with sulphuric acid and the sulphonic acid formed is reacted with sodium hydroxide.



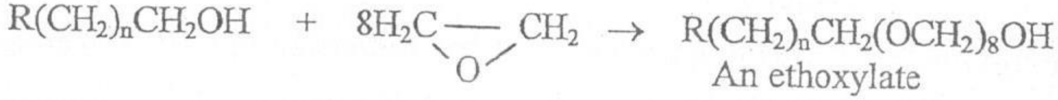
The detergent contains a number of methyl substituents and are not degraded (or broken down) by bacteria in the sewage plants. As a result, they cause foaming in rivers and lakes. In order to overcome the problem, straight chain alkenes have been used instead of the branched chain ones.

(a)



$$\text{(b) } RCH_2OH \xrightarrow{H_2SO_4} RCH_2\text{ - O- }SO_2OH \xrightarrow{NaOH} RCH_2\ SO_2\text{ - }O^- Na^+$$

(c)



Types of detergents

Detergents prepared by methods (a) and (b) are classified as anionic detergents since they contain ionic group as the hydrophilic components. Detergents prepared by method (c) are classified as non-ionic because they do not contain ionic groups. They are mainly used in liquid forms.

Cationic detergents are also known, for example, quaternary ammonium salts which are germicides.

Composition of detergents

A packet of detergent contains: active detergent (20%); sodium sulphate (20%) to increase the bulk of the powder; inorganic phosphates (30%), removes soluble complex calcium salts formed; sodium borate (ca. 5%), which acts as a bleach. Other ingredients used includes fluorescent organic compounds, which improves the appearance of clothes.

CHAPTER 16

POLYMERS

Introduction

Polymers are long-chain molecules with recurring structural units. The reaction which leads to the formation of polymers are called ***polymerisation,*** which can be defined as the building of large molecules by linking together of large numbers, often thousands, of small molecules called ***monomers***.

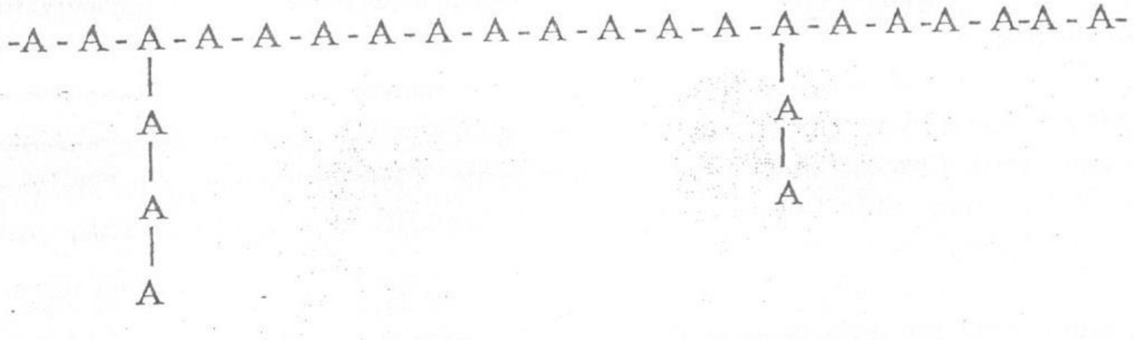
There are various ways in which monomer units can be linked together. For example, if A and B represent *repeating units*, the possible polymers formed are:

(a) -A - A -A - A - A - A - A - A - A - A - A - A - A - A - A - A - A - A - A - A-

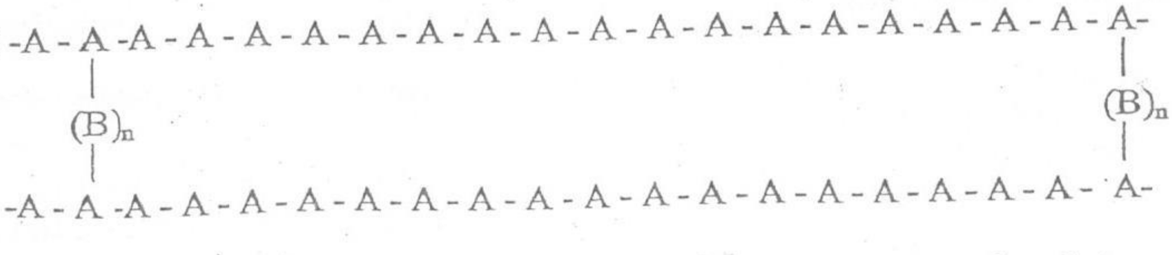
This is the simplest type of polymerisation. Monomer units are all the same type and are arranged in long chains.

(b) - A - B - A - B - A - B - A - B - A - B - A - B - A - B - A - B - A - B -

This is a variation of type (a) above where different monomer units are linked together.

(c)


In this type of polymerisation the chain can have either the same monomer or monomer of another type.

(d)


In this type of polymerisation, long chains are linked together by units of atoms

The size of polymers vary from one substance to another. A single specimen of a polymer will usually contain molecules of varying sizes. The molecular masses of polymers vary from few thousand to over a million.

Classification of polymers

Polymers may be classified as:

(a) ***Naturally occurring.*** For example: rubber, cellulose, silk, wool, keratin, etc.

(b) ***Man-made or synthetic polymers.*** For example: nylon, polythene, polyvinyl chloride, polyamides, polystyrene, etc.

Types of polymerisation

(a) Condensation polymerisation

Condensation polymerisation is brought about by the combination of usually two molecules with consequent elimination of small molecules, for example, water, ammonia or hydrogen chloride. The monomers normally contain two functional groups on the same molecule.

Examples

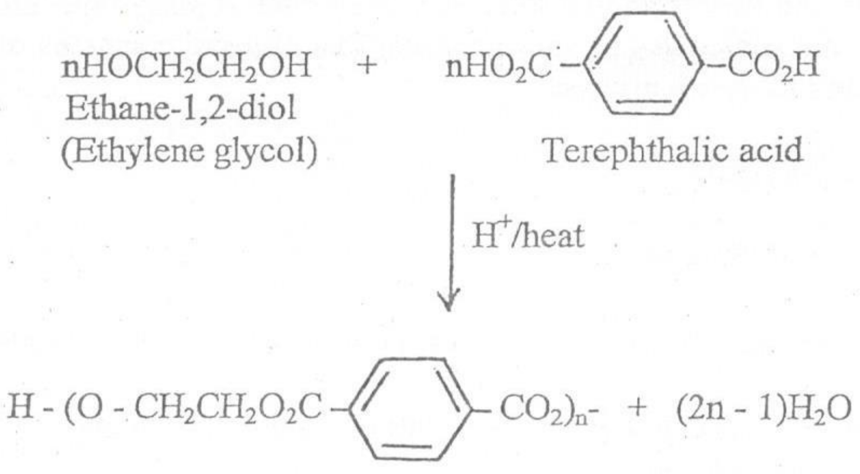
Formation of Nylon - 6,6.

$$\underset{\text{1,6-diaminohexane}}{nH_2N(CH_2)_6NH_2} \quad + \quad \underset{\text{hehanedioic (adipic) acid}}{nHO_2C(CH_2)_4CO_2H}$$

$$\Big\downarrow \text{heat}$$

$$\underset{\text{Nylon-6,6}}{H - [NH - (CH_2)_6NH - CO(CH_2)_4CO]_nOH} \quad + \quad (2n - 1)H_2O$$

Formation of Poly(ethene terephthalate) ('Dacron' or Terylene')



Poly(ethene terephthalate)
[Dacron or Terelyne]

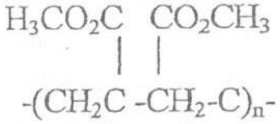
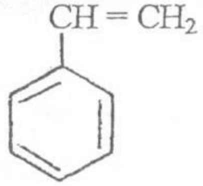
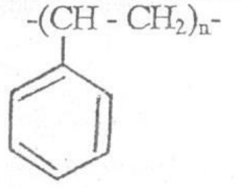
(b) Addition polymerisation

Addition polymerisation occurs by linking together or addition of a large number of small but unsaturated molecules. No other substances are formed during the reaction.

For example, formation of polythene

$$n(H_2C = CH_2) \rightarrow —(CH_2CH_2)_n—$$

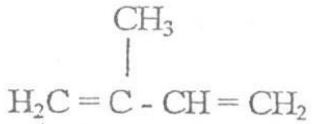
Other polymers formed by addition polymerisation

Formula of monomer	*Name of monomer*	*Polymer*	*Uses of polymer*
$H_2C = CH2$	Ethene	$-(CH_2CH_2)_n-$	Container, film, wrapping material
$H_2C = CHCl$	Chloroethene (vinyl chloride)	$-(CH_2CHCl)_n-$	Film, piping, insulations, leatherette (rainwear), records
$H_2C=C(CH_3)OOCH_3$	Methylacrylate	 $-(CH_2\overset{H_3CO_2C}{C}-CH_2-\overset{CO_2CH_3}{C})_n-$ 'Perspex' or 'Diakon'	Packing, lenses, aeroplane windows, corrugated roof lights.
$F_2C = CF_2$	Tetrafluoroethene	$-(CF_2 - CF_2)_n-$ Tetrafluroethene (PTFE)	Making seals and gaskets, surface coating for cooking equipment
$CH_3CH = CH_2$	Propene	$-[CH(CH_3) - CH_2]_n-$ Polypropene	Fibres, moulded articles
	Styrene (Phenylethene)	 Polystyrene	Packing materials, moulded objects, household goods e.g. combs, lining material for refrigerators

Rubber

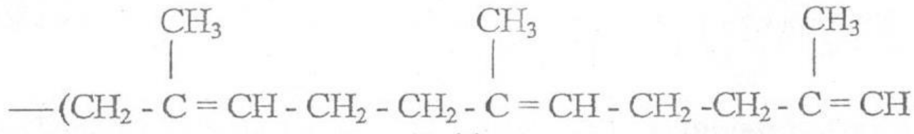
Natural rubber

Natural rubber is obtained from a latex of a tree, for example, *Hevea brasiliensis*. The latex is coagulated by the addition of ethanoic acid. The monomer of rubber is isoprene.



$H_2C = \overset{CH_3}{C} - CH = CH_2$

Isoprene
(2-methylbuta-1,3-diene)



$$-(CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2)_n-$$

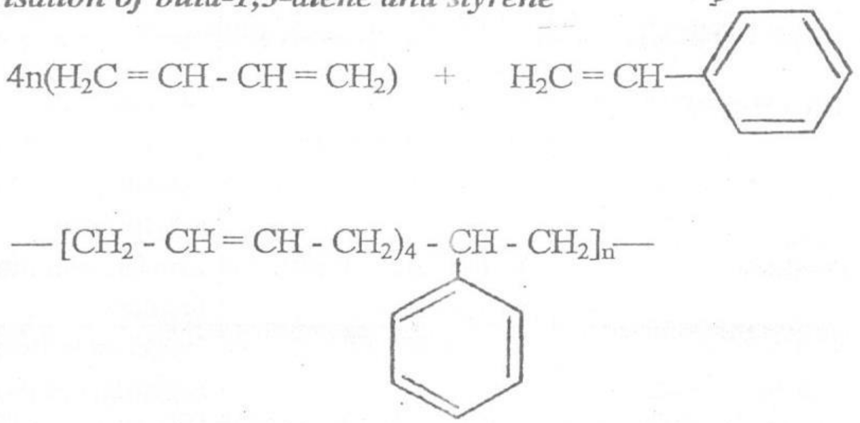
Rubber

The crude rubber is not strong enough nor is it elastic enough. To improve on its properties, the rubber is heated with a small amount of sulphur. The process is known as ***vulcanisation***. During the vulcanisation, the sulphur combines with the rubber, forming cross-linkage between carbon chains to give a product with better properties.

Synthetic rubber

Synthetic rubbers resemble natural rubber in that they contain double bonds in their polymer chains. Synthetic rubber may be made by the following processes.

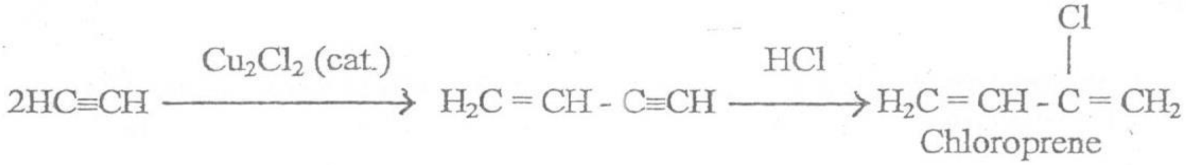
(a) Polymerisation of buta-1,3-diene and styrene



The polymer is called SBR (styrene butadiene rubber). The polymer is vulcanised by heating with sulphur and carbon black is added to increase its strength. The rubber is used in the manufacture of tyres, shoe soles, water proof boots and hoses.

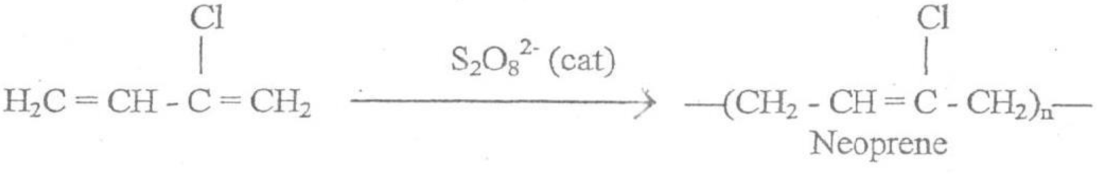
(b) Neoprene rubber is made by the polymerisation of chloroprene

Chloroprene, the starting material is prepared from ethyne.



$$2HC\equiv CH \xrightarrow{Cu_2Cl_2\text{ (cat.)}} H_2C=CH-C\equiv CH \xrightarrow{HCl} H_2C=CH-\overset{Cl}{\overset{|}{C}}=CH_2$$

Chloroprene



$$H_2C=CH-\overset{Cl}{\overset{|}{C}}=CH_2 \xrightarrow{S_2O_8^{2-}\text{ (cat)}} -(CH_2-CH=\overset{Cl}{\overset{|}{C}}-CH_2)_n-$$

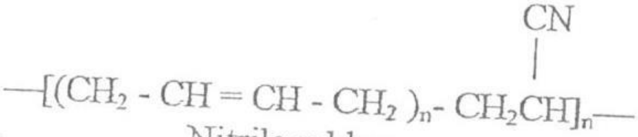
Neoprene

Neoprene is used in making hoses and gaskets.

(c) Nitrile rubber is made by copolymerisation of buta-1,3-diene and acrylonitrile

$$2nH_2C = CH - CH = CH_2 \quad + \quad nCH_2 = CH - CN$$

$$\downarrow$$



$$-[(CH_2 - CH = CH - CH_2)_n - CH_2\underset{}{\overset{CN}{\overset{|}{C}}}H]_n-$$

Nitrile rubber

Because it is very resistant to chemical attacks, nitrile rubber is used in making gaskets, oil seals and for making flexible fuel and oil tanks.